ABSTRACTS

INTERNATIONAL SEMINAR ON HIGH ENERGY MATERIALS (HEM)

(19-21 NOVEMBER 1996)

AT

High Energy Materials Research Laboratory (HEMRL)

Sutarwadi, Pune-411 021, INDIA



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High Energy Materials Society of India (HEMSI)



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INVITED TALKS

- 1. A review of the Thermal Decomposition pathways in RDX, HMX and other closely related cyclic nitramines Dr. S. Bulusu, U.S.A.
- 2. Surface Pyrolysis of High Energy Materials Prof. L. De Luca, Italy
- 3. Performance increase of Propellants with new energetic compounds Prof. F. Volk, Germany
- 4. Combustion of Hybrid rocket propellants Prof. R.P. Rastogi, India
- 5. Resolved Optical Spectroscopy of Energetic Material Decomposition under static high pressure Dr. T.P. Russel, U.S.A.
- 6. Recent Advances in the field of Gun Propulsion Shri P.U. Deshpande, India
- 7. Mathematical modelling of combustion of propellants Prof. A.M. Lipanov, Russia
- 8. Thermal stabilization of Ammonium Dinitramide (ADN) Dr. I.B. Mishra, U.S.A

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NITRAMINE-BASED GUN / ROCKET PROPELLANTS

COMBUSTION MECHANISM OF A LOVA PROPELLANT

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An experimental and theoretical analysis is conducted of the steady burning properties of energetic LOVA materials. In particular, a composite solid propellant made of RDX and HTPB binder was tested over the pressure interval from 1 to 81 atm under nitrogen atmosphere. Thermophysical and thermochemical properties were deduced by properly combining steady burning rates and temperature profile measurements, respectively obtained by TV recording and microthermocouples (or combination of both). The thermal analysis was conducted with special microthermocouples furnished by Prof. A.A.Zenin (Semenov Institute of Chemical Physics, Moscow, Russian Academy of Sciences) and at least initially during this experimental program, in close cooperation with him. The apparent value of activation energy for pressure dependent surface concentrated gasification is deduced. Measurements of condensed phase characteristic thicknesses for both the solid and multiphase (liquid + residual solid + bubbles of gases) layers below the burning surface are reported vs pressure. The sensible temperature dependence of the RDX specific heat and to a lesser extent, density are taken into account when evaluating thermal diffusivity. Values of thermal conductivity are based on experiments conducted for pressed RDX powders. Measurements of steady thermal gradients at the burning surface vs pressure and thus evaluation of the thermal fluxes both from the gas phase side and to the condensed phase side, manifest the melting effects of RDX crystals in the condensed phase and a double flame structure in the gas phase. In general, burning of RDX-based propellants involves a complex set of reactive phenomena with multiphase, multidimensional, transient features on a microscopic scale. The detailed analysis of energy fluxes proves that decomposition starts in the condensed phase by endothermic processes (perhaps even before liquefaction), carries on by exothermic processes first in the molten layer and later in the gas phase. Steady dependencies of burning rates, surface temperatures, flame temperatures, and other parameters (when available) on pressure are then compared with measurements performed for several RDX-based solid propellants in a variety of international laboratories. Agreements and discrepancies are discussed.

Following this overview of thermophysical and ballistic properties, the intrinsic stability of burning of several RDX -based propellants is theoretically investigated and numerically verified. The linear stability boundaries of the familiar time invariant steady-state combustion are rigorously deduced for both pressure and/or radiation-driven burning. In addition, the approximate nonlinear boundaries of the self-sustained steady state oscillatory combustion are evaluated. The latter ones take the meaning of deflagration boundaries, since beyond them steady state combustion is no longer allowed. The effects of several parameters, in particular of temperature dependent thermophysical properties, on both boundaries are discussed. Numerical simulations in general confirm the analytical expectations.

STUDIES ON OXIDIZERS FOR LOW VULNERABLE AMMUNITION (LOVA) PROPELLANTS

M.K.Choudhri, S.B.Pawar, M.P.Kulkarni and S.N.Asthana High Energy Materials Research Laboratory, Pune (India)

LOVA system is gaining importance as futuristic propellants for guns. Attempts are on all over the world to optimize the properties of these low vulnerable systems to achieve dual objectives of low flame temperatures and higher energetics. We have earlier reported the energetics and sensitivity data obtained for RDX, HMX, DATB and HNS based LOVA with CAB binder. This paper reports the studies conducted on LOVA compositions containing oxidizers such as Nitroguanidine, triaminoguanidinenitrate (TAGN) and dinitro piperazine (DNP) in combination with RDX. The oxidizers were evaluated in 80% concentration in CAB-based LOVA propellants. Thermodynamic computation of formulations was done by applying NASA code to determine the properties namely, adiabatic flame temperature, molecular weight of reaction products, number of gas moles generated per gram of propellant, covolume of reaction species, specific heat ratio, gas volume and percentage composition of combustion products. The practical data on energetics was obtained in closed vessel at 0.1 g/cc loading density. The sensitivity of these LOVA formulations to various stimuli, like impact, friction was also determined along with their ignition temperature during this study. The thermal decomposition pattern was obtained by DTA.

Theoretical calculations reveal that the adiabatic flame temperature of compositions containing 80% RDX or HMX is 2772 K and 2740 K respectively which are considerably less than that of conventional propellants like M-30, NQ or F-528/427; while energetics (impetus) of these formulations were superior or equal to those of conventional propellants, except F 528/427 which has higher impetus (1236 J/g) but at the same time, very high flame temperature (3688 K), which is detrimental from gun erosion point of view.

Compositions containing Nitroguanidine, DNP and TAGN gave flame temperatures of 1278, 924 and 1614 K respectively whichare considerably less than that of even RDX based formulation. However, their energy (impetus values 526, 584 and 800 J/g respectively) is about one-third of RDX-based LOVA composition. In view of their low energy but attractive flame temperature, wehave developed compositions containing these oxidizers in combination with RDX. 10 and 20% replacement of RDX by DNP gave flame temperatures 200 to 500 K less (2547 & 2223 K respectively) with impetus 100 J/g less as compared to compositions containing 80% RDX. Similar is the case with TAGN and nitroguanidine when used as additive (10-20%). However, the impetus of these compositions is comparable to that of conventional M-30 propellant with the added advantage of lower flame temperature. These results suggest the practical importance of these compositions. The studies carried out during this work reveal that all these LOVA compositions are less sensitive to impact (height of 50% explosion is 93-170 cm) and friction (no explosion with the load of 17-36 kg) and their thermal decomposition temperature (Ignition temperature 218-265°C) is higher than their conventional counterparts as well as RDX-LOVA. All the formulations studied have higher specific heat ratios and covolume of the gases than the conventional propellants. This is due to lower molecular weight of their combustion products. Gases with high specific heat ratio tend to cool faster leading to slightly decreasing energy whereas higher covolume can be used to increase the ballistic efficiency of the system when properly coupled with programmed burning.

As LOVA propellants are known to have ignition problem, apart of RDX (10 & 20%) was replaced by oxygen-rich ammonium- and potassium perchlorates. The effect of these additives on energetics and sensitivity was also evaluated in this work.

SYSTEMATIC STUDIES ON THE USE OF BIMODAL RDX IN LOVA FOR GUN PROPELLANT APPLICATIONS

M.M.Joshi, C.R.Dayanandan, A.G.S.Pillai, B.R.Gandhe and J.S. Karir High Energy Materials Research Laboratory, Pune (India)

The energy level of LOVA gun propellant depends upon the per cent loading of nitramine in the formulation. It is known that the burning behaviour depends upon the particle size of nitramine used in the propellant. The data on bimodal RDX-based LOVA gun propellant is scarce and so far a few systematic studies have been carried out on formulations based on bimodal RDX with respect to variation in the proportion of fine and coarse particles in a given system. Two series of the LOVA gun propellant formulations based on RDX/CA/NC/DOP and RDX/CA/NC/TA compositions, with varying proportion of 5 and 20 micron RDX from 100 : 0 to 60 :40 keeping overall quantity of RDX at constant level (77%) were processed for the present studies. The percentages by weight of each ingredient in all the formulations was bimodal RDX : 77% binder system : CA 13%, TA or DOP, 6%, NC (N : 12.2%) 4%.

The batch size in every case was 2 kg. The sigma blade incorporator (5 lit. capacity) was used for mixing the ingredients. The propellant dough was extruded into heptatubular strands with the help of a vertical hydraulic press using a suitable die-pin assembly. The strands after drying were cut into grains of suitable size (L/D 2.3 ± 0.2). All the propellant formulations were processed under identical conditions and the grains had the same geometry (heptatubular) and length-to-diameter ratio (2.3 ± 0.2). The C.V. firing data were obtained using same igniter powder in all the cases and the propellant samples conditioned at room temperature (27° C) were used in all the experiments.

It is observed from the data obtained that pressure exponent (α), linear burning rate coefficient (β_1), dp/dt and vivacity of the propellant are greatly influenced by change in particle size proportion. However, the extent of the change of these parameters appears to depend on chemical composition of the propellant. Thus, for example, α value changes from 0.97 to1.61 in the case of DOP-based propellants as the ratio of fine-to-coarse RDX in bimodal RDX is varied from 100:0 to 60:40 but in case of TA based composition variation in α for the same change in proportion of fine-to-coarse RDX is only from 0.8 to 1.05. This trend was observed in the case of β_1 values also.

The burning rate (r) and average vivacity of the propellants were found to increase with increase in the percentage of 20 μ particles at the cost of 5 μ particles. Herealso, like other parameters, rate of increase is much higher in the case of RDX/CA/DOP/NC based propellants than for RDX/CA/TA/NC based propellants.

The data on burning rate coefficient (β_1) and pressure exponent (α) for propellants of both the series indicate that by making use of bimodal RDX of optimum proportion of sizes it is possible to modify the burning behaviour of LOVA propellant so as to achieve the desired values for α and β_1 . Thus, for example, in the case of RDX/CA/NC/TA based composition the optimum ratio of 5 micron to 20 micron size RDX appears to be 80 : 20.

The comparison of results on ignition temperature, impact sensitivity and friction sensitivity for the unimodal and bimodal RDX and propellant NQ shows that RDX based propellants studied during this work are less vulnerable to heat, impact and friction than the conventional propellants like NQ.

STUDY OF ENERGETIC NITRAMINE BASED EXTRUDED DOUBLE BASE (EDB) PROPELLANTS

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Incorporation of cyclic nitramines (RDX/HMX) in double base matrix enhances the energy output by virtue of their favourable heat of formation in addition to other advantages viz. better thermal and chemical stability, low signature and superior insensitivity to shock. However, these propellants show relatively low burn rate and high pressure index value.

Literature survey on nitramine propellants reveals that appreciable data on slurry cast nitramine based composite double base propellants are available but scanty information on nitramine based extruded double base (EDB) propellants is reported. Keeping in view these facts, a number of RDX based EDB formulations, primarily based on low and high call vall with and without ballistic modifier have been processed and studied systematically for various parameters such as sensitivity, thermal, chemical and mechanical properties and burn rate. The generated data have indicated that (i) increase in RDX concentration beyond 15% drastically reduces the mechanical properties and thus formulation containing RDX (10%) is considered promising for both types, (ii) pressure index value 'η' for low call val (870 cal/g) as well as high call val (1060 cal/g) compositions with 10% RDX, in the pressure range of 35-90 kg/cm² are of the order of 0.73 and 0.60 respectively and (iii) in the presence of ballistic modifiers, 'η' values of both the formulations have been reduced significantly.

HTPB-BASED COMPOSITE PROPELLANTS

MIGRATION OF CHEMICAL SPECIES IN HTPB-XT PROPELLANTS

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Hydroxyl terminated polybutadiene (HTPB) resin based solid propellants are being currently used in ISRO launch vehicles. SPROB had taken up the study of extended HTPBs for the purpose of enhancing the pot life of the propellant slurry and developed a HTPB-XT resin to overcome the problems of shorter pot life of present HTPB propellants. The migration of chemical species in the HTPB-XT propellant was studied. Analog cartons simulating the propellant of main motor were planned with 120 kg mix level propellant and subjected to ageing at room temperature as well as at elevated temperature (accelerated ageing). Aged samples were drawn at regular intervals over a period of 100 days. Samples from cartons were subjected to soxhlet extraction and analysed for concentration of chemical species in insulation rubber as well as in propellant. Similarly, the migration of chemical species in the propellant collected from Agni motor after a fixed time was determined and compared with normal HTPB propellant. The change in concentration of species from the insulation to interior propellant was also studied and compared with HTPB propellant. The interesting aspect of the paper is to deal with the migration of other chemicals alongwith usual plasticizer.

EFFECT OF CRYSTALLISATION CONDITIONS OF AMMONIUM PERCHLORATE ON FRIABILITY AND ITS CORRELATION TO BURN RATE

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Ammonium perchlorate (AP) is the main oxidiser in solid composite propellants. AP manufactured by different chemical routes is chemically same and it also had the similar type of particle size distribution. However, it may not be possible to get similar ballistic properties by using same proportion of AP in composite propellants manufactured by different routes. It shows mainly deviation in burn rate characteristics. To explain the difference in burn rate, the friability of AP was studied. Another factor contributing to this burn rate deviation is the difference in crushing load of AP crystal manufactured by different routes. The low crushing load may be susceptible to size reduction during kneading while processing the composite propellant leading to particle size reduction which affects the burn rate. The crushing load of the crystal and its friability mainly depends on the crystallisation conditions of AP. The burn rate deviation could probably be explained due to friability and crushing load condition.

EFFECT OF MIXING EFFICIENCY ON VISCOSITY AND MECHANICAL PROPERTIES OF HTPB-BASED POLYURETHANE SOLID PROPELLANTS

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Hydroxy terminated polybutadiene (HTPB) is widely used as binder for Composite Solid Propellants due to advantage of high solid loading capacity, convenient viscosity of slurry for casting and high fuel value. Modality of making solid propellant involve preparation of premix by taking liquid ingredients (other than curator) such as HTPB, internal and external plasticizers and subsequent mixing with ammonium perchlorate (AP) and aluminium powder (Al). Final mixing involves incorporation of curator viz. toluene diisocyanate. Mixing should be efficient to have uniform distribution of all ingredients and sufficient unloading viscosity followed by buildup. Effect of mixing intensity on efficiency of mixing, unloading viscosity, viscosity build-up and mechanical properties of cured propellant have been studied during this work. Intensity of mixing is calculated from power input, diameter of the blade, number of rotations of the blade and time of mixing. Effect of mixing as a function of homogeneity of propellant, unloading and build-up of viscosity of propellant slurry as well as mechanical properties and burn rate of cured propellant have been studied. Though the mixing could be efficient as seen from homogeneity data, further mixing was needed for highly solid-loaded propellant to achieve lowest unloading slurry viscosity and minimum dispersion of mechanical properties as well as burn rate for cured propellant.

REGRESSION RATE STUDY IN HTPB/GOX HYBRID ROCKET MOTORS

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Rocket propulsion concept in which one of the two components (oxidizer and fuel) of propellants is stored in liquid phase while the other is stored in solid phase is called hybrid propulsion system. The combination of a solid fuel and liquid oxidizer is most common and referred to as the classical hybrid rocket. The important advantages such as lower potential cost and safer operational characteristics of hybrid rockets over those of conventional solid and liquid propellant rockets generated the interest in hybrid rockets for launch applications (1). The dependence of solid fuel regression rate on various operating conditions is an important aspect in the study of hybrid rocket propulsion.

In the 1960's Maxman et al (2) developed a regression rate model under the assumption that the regression rate is controlled by the heat transfer to solid fuel from the flame zone within the boundary layer. The regression rate is dependent on oxidizer mass flux, temperature, pressure, fuel port geometry and fuel composition. But oxidizer mass flux is the major variable that determines the regression rate and the widely used regression rate correlation is, r = a Gov. So many differences exist in the various regression rate models and the experimental correlations developed so far. With the aim to facilitate the development of large scale hybrid rocket motors, an experimental research is initiated at IIT. Madras with the objectives of enhancing our understanding of the boundary layer combustion processes and critical engineering parameters that define such processes. The fuel used in this study is HTPB and the oxidizer is gaseous oxygen. A high pressure hybrid rocket motor test facility and a high pressure (40 bar) axisymmetric subscale motor is designed and fabricated for conducting experimental investigation. The gaseous oxygen supply is from a bank of cylinders at a maximum pressure of 150 bar. A manually operated ball valve is used to initiate and terminate the flow of oxygen and a typical nozzle placed in the oxygen pipe line maintains steady mass flow rate. A pyrogen type igniter initiates combustion. Gaseous nitrogen is used as purge gas to terminate combustion after the desired burning time. The pressure maintained upstream of the nozzle is three times higher than the maximum combustion chamber pressure, so that oxidizer mass flow rate is constant during each test. The ability to test hybrid motor under high oxidizer mass flux 60 g/cm².s (a typical value for actual systems) is the speciality of the test facility.

The measurements undertaken during the experiments are pressures at upstream and downstream of the nozzle, aft mixing chamber, combustion chamber of the pyrogen igniter and thrust. All the signals from strain gauge type pressure and thrust transducers are recorded in an IBM PC AT using a data acquisition system. The averaged solid fuel regression rate is determined by weighing the fuel grain before and after each test. Using a data reduction code, instantaneous regression rate is estimated from the experimental measurements. The test variables are oxidizer mass flux, port diameter and grain length. Fuel grains of two different initial port diameters and three different length-to-diameter ratios are tested. Tests are also carried out with grains containing small quantity (< 5%) of solid oxidizer (ammonium perchlorate) as an additive. The additive is expected to increase surface/sub-surface reaction and hence regression rate.

The effects of the grain geometry and the additive on fuel regression rate are discussed in this paper.

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ECO-FRIENDLY PROPELLANTS

TECHNICAL LIMITS OF USING ATOMIC HYDROGEN, METALLIC HYDROGEN AND ELECTRONICALLY EXCITED HELIUM AS ROCKET PROPELLANTS

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Among the advanced rocket propellants that have been discussed in the last decade are Atomic Hydrogen, Metallic Hydrogen and Electronically Excited Helium. Their potential I_{sp} is so much above the theoretical limits of today's propellants (about 500 s for LOX/LH₂ under ideal conditions) that they could revolutionise space transportation.

Unfortunately, these propellants are highly reactive under normal conditions and hence their potential I_{sp} has a price that must be paid through extreme efforts in production, stabilisation and storage techniques involving very strong magnetic fields, very low temperatures or very high pressures respectively. The details are discussed in the paper.

The design of appropriate propulsion systems is mainly determined by these constraints. Alternative concepts are presented and discussed, reflecting the current status of basic research. The feasibility of the propellant concepts and their chances for future application are compared and evaluated.

DEVELOPMENT OF PROPELLANTS CONTAINING AMMONIUM NITRATE

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Ammonium nitrate has always been an interesting oxidizer in the field of propellants. The substance is cheap, readily available, burns smokeless in metal-free formulations without developing HCl and creates no ecological problems. The drawbacks of AN are its hygroscopicity, phase transitions under storage conditions, low burning rate and lower performance compared with ammonium perchlorate formulations. The demand for smokeless, insensitive and less polluting propellants has led to continued research for understanding and improving the properties of AN and for finding acceptable propellant formulations with AN as oxidizer.

For understanding the phase properties of AN the classical tools of thermal analysis had to be complemented by time and temperature resolved X-ray diffraction for obtaining unambiguous results. Application of Rietveld refinement to the X-ray diffraction patterns opens new possibilities of gaining detailed information on the lattice dynamics.

According to literature, potassium and cesium stabilize the phases III and II, respectively. A working hypothesis was deduced assuming that smaller cations stabilize phase III, whereas larger cations stabilize phase II. Using transition metal complexes as larger cations the phase properties of AN could be improved.

To satisfy the demand of larger quantities of AN for propellant development, a pilot plant was built up for the production of spherical particles suitable for propellant formulations including pure AN as well as material stabilized with complexes of Cu, Ni and Zn.

The propellants studied were based on AN and GAP as an energetic binder. Thermodynamic calculations showed that non metallized formulations need energetic plasticizers for realising the desired value of 240 s for the specific impulse. Therefore, BTTN and TMETN were included in the formulations. The initially poor combustion properties of the formulations could be improved by optimizing the particle size distribution and by developing a new catalyst. Propellants with pressure exponent ranging from 0.49 to 0.58, burning rates ranging from 7-8 mm/sec and a specific impulse of 230-235 s were formulated during this work. The requirements for chemical stability created severe difficulties that could be eased by suitable stabilizers. The resulting materials fulfil the requirements for less sensitive propellants.

BURN RATE STUDIES ON AN-BASED PROPELLANTS : EFFECT OF N-N BONDED BINDERS

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Increasing emphasis on clean burning propellants has led to a renewed interest in ammonium nitrate (AN)-based solid propellants. The innocuous nature of the combustion products of AN and its low cost as well as easy availability, make it an attractive oxidizer. Major problems involved in its use till a few years back, were its phase transformation at room temperature involving a volume expansion, hygroscopicity and low burn rate. Of these, the first two problems have been overcome in recent times. By cocrystallizing AN with KNO₃ the phase transformation has been subdued and shifted away from the ambient temperature. The hygroscopicity can be managed by coating the AN particles with hydrocarbons/polymers. The low burn rate problem, however, still persists. Our recent studies on the use of newly synthesised N-N bonded epoxy resins as binders, in ammonium perchlorate-based propellants revealed an enhancement in the burn rate of the order of 4 to 5 fold. It is interesting, therefore, to examine if the burn rate of AN-based propellants is also affected in a similar way, by the use of N-N bonded epoxy binders.

The investigation reports an improved method of making the N-N bonded resins. Synthetic parameters and chemical characterization data on four diglycidyl amine-epoxy resins based on carbono and thiocarbonohydrazones have been obtained. Propellants based on AN have been processed with 80% solid loading using these resins as binders. The burn rate data, as determined using a strand burner reveal a marked increase as compared to that processed using a conventional butadiene binder, with virtually no residue. Inclusion of small percentage of magnesium powder into the propellant composition results in further enhancement in the burning rate. An explanation in terms of enhanced combustion reactivity of N-N bonded binder with AN, an acid producing oxidizer and a probable synergistic effect in the presence of magnesium is advanced.

OF PHASE STABILISED AMMONIUM NITRATE (PSAN)-AN ECO-FRIENDLY OXIDIZER

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Composite propellants based on ammonium perchlorate (AP) as oxidizer are state-of-the-art systems. However, global environmental impact restricts AP-based propellants because of its HCl exhaust. Therefore, efforts are on to innovate propellants with clean exhaust. Consequently, ammonium nitrate (AN) has regained interest in the field of propellants and explosives, more specifically insensitive formulations, because of its clean burning and low hazard. But, its dimensional instability caused by enantiotropic nature and extreme hygroscopicity makes it difficult to use AN as an ingredient in solid propellants. Many approaches have been made to solve this problem.

Phase Stabilised Ammonium Nitrate (PSAN) was prepared in our laboratory by incorporating copper (II) diamine nitrate in the AN crystal lattice, thereby avoiding the abrupt volume change within the useful temperature range. However, the energetics of the PSAN-based propellant are not that encouraging and therefore warrant incorporation of high energy materials like RDX or HMX. As a preliminary evaluation to assess the effect of an energetic material, we undertook a study on the thermal behaviour of PSAN with RDX as an additive using thermogravimetry (TG) and differential scanning calorimetry (DSC).

Decomposition temperatures of PSAN and RDX are almost in the same temperature range. The synergetic exothermic interaction between PSAN and RDX resulted in a net exothermic reaction of the PSAN. This is a positive indication of the overall enhancement of the energetics of the system. The kinetic and thermodynamic parameters for the decomposition process were evaluated. The activation parameters were computed by Ozawa and Kissinger methods. The activation energy obtained by Ozawa method was refined by an iteration procedure using the two term approximation for Arrhenius temperature integral p(x). The kinetic parameters obtained from the two methods are found comparable. Investigations on the effect of HMX on PSAN decomposition are in progress.

FUEL-RICH PROPELLANTS

VELOCITIES OF REACTING BORON PARTICLES IN A SOLID FUEL RAMJET COMBUSTION CHAMBER

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The addition of boron particles to a solid fuel for ramjet engine is of interest because of its high volumetric heat of combustion. Unfortunately, a rapid and complete combustion of these particles is obstructed by the formation of a liquid boron oxide layer, that covers the surface of the particles after their ignition. Only at higher temperatures this layer might be vaporized. So these particles must be heated up relatively quickly inside the combustion zone in relation to their residence time inside the combustion chamber.

In order to get a better understanding of the movement of the particle phase in relation to the diffusion flame and mode of their emission from the solid fuel surface, 2-dimensional LDV measurements have been conducted in a two dimensional dump combustor of 200 mm length, 150 mm width and 45 mm height. Quartz windows on both sides allow the optical access. Hot air vitiated by H_2/O_2 -burners has been used for the combustion of the boron containing solid fuel slabs with 100 mm width, which are positioned directly behind the flame holder step of 20 mm height. Hydroxyl-terminated polybutadiene (HTPB) with boron particles of a nominal diameter of 1-2 μ m has been chosen as solid fuel. A constant nitrogen stream in front of the windows protects against soot and particle deposition. Test configurations used are given below:

		Outer flow	1	2
		•	not seeded	seeded
a	Solid		х	х
b ·	Fuel	30% Boron	x	x
С	with	5 % TiO ₂	x	x
d		5% TiO ₂ and 25% Boron	x	х

Test runs with and without boron have been done. HTPB gave no LDV signal at all, when burnt without boron particles. To get velocity data of the combustion process without boron, TiO₂ particles were added to the solid fuel. Velocities above the flame zone were measurable by seeding the hot air stream entering the combustor with TiO₂. With the ability of seeding either the solid fuel or the outer flow or both it was possible to show whether the combustion of boron particles changes the mean velocity field.

Test cases 1a,b,c,d mainly were chosen to see whether the velocities of the boron particles and the velocity of the gas phase are different i.e. whether different velocities for seeding the solid fuel with boron and/or TiO₂ can be measured. The results show similar values between set-ups 1b, 1c and 1d. Slightly lower mean velocities were found in the absence of boron. Configuration 1b, without seeding of the vitiated air, was also used to determine the boundary of the visible flame zone and to investigate the intrusion of boron particles into the outer flow. Beyond that boundary, only a few boron particles were found giving a data rate too small for LDV measurements in that arrangement. The boundary detected with LDV seems to coincide with flow visualisations by video recordings.

During each run the lower wall boundary of the combustion chamber given by the solid fuel lowered within 3 minutes by about 10 mm. This had to be taken into account and it was found that within the first 2 minutes of burning

time the velocity profiles kept almost constant. To characterize the velocity field in the combustion chamber, flow configuration 2b was used. The data rate for solid fuel with boron only was sufficient for reliable results. Therefore, no additional seeding of the solid fuel was necessary and the mass fraction of boron is not required to be changed.

The velocity field shows a strong 3-dimensional structure, though the inlet velocity distribution at the flame holder step was found to be 2 dimensional. The measurements suggest that two counter revolving eddies exist which also affect the local regression of the solid fuel slab.

The results showed that the boron particles follow the velocity field of the gas phase in a similar way as TiO₂ particles which were added to the solid fuel i.e. the burning of the boron particles does not seem to affect their velocities as well as path.

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EFFECT OF AGGLOMERATION ON COMBUSTION OF METALLIZED PROPELLANTS FOR AIR-BREATHING PROPULSION SYSTEM

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Theoretical evaluation of thermochemical properties of fuel candidates for advanced air-breathing propulsion system shows that metallic fuels have superiority in comparison to hydrocarbon fuels due to their high energy and high density. In spite of the promising potential, the metallized propellants present severe problems of complex burning phenomena which have major effect on the energy generation process within the combustor. This is mainly due to agglomeration of the metal particles at the burning surface prior to their ejection into the gas stream depending on the nature of the metal used and the properties of its oxide. This paper presents an extensive study carried out on the metallized propellants containing metals viz Mg, Zr, Al, B and as oxidiser NaNO₃ in order to find out variations in energetics and burning rate properties at different oxidiser levels and for different particle sizes of the ingredients.

The study indicates that heat energy of the formulations increases when the composition approaches from fuel-rich to stoichiometric value irrespective of the particle size of the ingredients but the burning rate follows different pattern. Burning rate of Mg-NaNO₃ and Zr-NaNO₃ compositions with finer size NaNO₃ shows higher values at lower oxidiser content and decreases with increasing concentration of the oxidiser. In contrast, Al-NaNO₃ and B-NaNO₃ formulations show continuous increase in burning rate with the increased oxidiser content. Further, the burning rate of all the formulations with coarser size NaNO₃ was found to increase on increase in the oxidiser content.

Thermal decomposition results indicate that the reactions occurring at the burning surface and/or in the vapour phase diffusion zone depending on the nature of the metal oxide and the degree of the metal agglomeration, are responsible for the variations in the burning rate.

In the case of Mg and Zr formulations, decomposition products of finer size NaNO₃ formed before melting/ignition temperatures of the metal particles, react exothermically with the metal particles for condensed phase/surface heat release. This heat release having higher value at lower oxidiser content leads to a thicker oxide coating on the metal particles leading to formation of metal agglomerates which burn inefficiently in the vapour phase causing lower burning rate. With coarser size NaNO₃, reactions shift to the vapour phase diffusion zone due to its decomposition after the attainment of melting/ignition temperature of the metal particles. This explains why the burning rate increases in the case of Mg and Zr as the particle size of NaNO₃ increases.

Combustion of Al and B particles occurs after melting/ignition temperature of the metal particles is reached without any surface reactions. This is because of the presence of protective oxide layers around the metal particles leading to vapour phase combustion at all the oxidiser concentrations in the case of Al and B unlike for Mg and Zr where porous oxide layer is present. This causes an increase of burning rate with increasing oxidiser content. However, the increase of particle size of the oxidiser lowers the burning rate of Al and B due to long residence time of the molten layer of the oxidiser at the burning surface resulting in the increased degree of metal particle agglomeration.

The study carried out by the authors has indicated that Mg-and Zr-based fuel-rich formulations in the presence of finer NaNO₃ provide a highly combustion efficient composition for air-breathing propulsion system in comparison to Al and B.

STUDIES ON PERFORMANCE OF FUEL-RICH PROPELLANT FORMULATIONS

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Selection of propellant formulation is dependent on the satisfactory performance of the propellant in the mode and mission in which it has to function. In air-augmented propulsion system, outside air is used as oxidiser and the propellant is highly fuel-rich and thus predicted specific impulse values are around 1000s in secondary mode. However, satisfactory ignition, sustained combustion and efficient expulsion play a vital role in realizing the predicted performance. Fuel-rich propellants either function as gas generating propellants in ducted ramjets (DRJ) or as solid fuels in solid fuel ramjets (SFRJ). In ducted systems further modification in the design is made by incorporating a variable flow rate system at the exit nozzle of the primary chamber to improve performance further. The requirement of propellant characteristics in these applications differ. Good ignitability both in primary and secondary chambers and efficient expulsion are the prime concern in DRJ mode whereas high fuel value and ease of decomposition of the fuel are decisive in SFRJ applications. In variable flow ducted rockets (VFDR), higher pressure index for the propellant is an additional design requirement. Various formulations are proposed and studied by research workers to meet these specific demands on propellant performance. The objective of the present study is to develop formulations based on a hydroxy terminated block copolymer for use in advanced VFDR and SFRJ. The block copolymer used in the study is compatible with nitric ester plasticisers and is prepared from hydroxy terminated polybutadiene and caprolactone. The study reports the calculated energetic parameters and also initial findings on the ignition and combustion behaviour of the propellant formulations.

Performance prediction for all the formulations has been made using NASA-271 computer program. Calorimetric and calorific values have been calculated using reported values for the propellant ingredients. Formulations have been processed using 5 litre capacity planetary mixer. Ignition and combustion data have been generated by burning

propellant strands in air or in test motor in primary mode.

Theoretical specific impulse increased with increase in fuel value. Highest value of 1000s was obtained with block copolymer processed using only inert plasticisers. Polymer processed in this way was found to have excellent elastomeric properties and thus can be a good candidate in SFRJ applications. Ignition studies showed that this formulation as such cannot be ignited in primary mode and thus some amount of oxidiser is essential for application in ducted mode. Incorporation of energetic plasticizers like nitroglycerine improved the ignitability and combustion stability in primary mode. Calorimetric (calculated) value increased with increase in energetic plasticiser in the formulations. Compositions having calorimetric value of 100-200 cal/g exhibited good ignitability and sustained combustion both in strand burning and motor firing. Modification in combustion characteristics was achieved by incorporation of minor amounts of metal and energetic additives. The formulation is flexible and can be further tailored to suit specific requirements of VFDR mode.

INVESTIGATIONS ON SUPERSONIC HYDROGEN COMBUSTION WITH TRANSVERSE INJECTION BEHIND A REARWARD-FACING STEP

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Futuristic missiles and space launcher propulsion systems will be dependent on air-breathing systems due to their high specific impulse. Supersonic Combustion Ramjet engines are currently under active development for the propulsion of hypersonic vehicles due to their attractive potential. Serious research is underway to achieve an improved understanding of the physical phenomenon present when supersonic flow undergoes chemical reaction. The flow through the combustor is continuous, supersonic and is composed of mixing and burning of fuel and air. The fuel injection, mixing and ignition parts are extremely important and in diffusion controlled combustion they control heat release. The most difficult problem areas in the design of SCRAMJET engines are associated with the combustion process. In supersonic combustor, the fluid transit time keeps going down and reaction will not go to completion and combustion efficiency will be much less. An extremely important requirement of such combustors is very rapid mixing, ignition and reaction so that excessive length is not required and hence excessive weight, drag and cooling requirement can be eliminated.

In order to carry out the experiments essentially required for the development of Supersonic Combustor and to clearly understand the various complex areas associated with it, there is a need of Supersonic Combustion test facility. A Hydrogen burner is chosen and designed for the facility to produce the test gas in which high temperature main stream test gas is produced by the combustion of hydrogen, oxygen and air in a burner. The hot gas from the burner, called vitiated air, contains oxygen in a volume fraction equal to that of air, simulating the flight conditions of Mach 5 upto 25 km altitude with combustor entry Mach No. of 1.67. Using this vitiated air, a two dimensional combustor is used for experimental investigations. Combustor is provided with constant area followed by a divergent portion with 2°divergence in side walls. A rearward-facing step is used on the top and bottom walls of the combustor in the constant area section for flame stabilization. Hydrogen fuel supply to the combustor is arranged in such a way that fuel is injected at upstream and downstream of the step, known as pilot and primary injections. Strain gauge type pressure transducers and miniature 'R' type of thermocouples are respectively used for pressure and temperature measurement. In each test run, twenty five parameters are recorded through a data acquisition system and a closed circuit TV is used for visual observation of hydrogen flame.

In the first part of the investigation the performance of Hydrogen burner is studied by conducting a number of tests. The main objective of these tests was to determine the burner performance in terms of stagnation temperature and pressure required corresponding to the flight conditions. A two dimensional nozzle designed for Mach 1.67 condition is attached with the burner and burner stagnation pressure, nozzle exit pressure and variation of burner stagnation temperature with different mixture ratio are studied. The theoretical and experimental results are compared and it is observed that they are in good agreement.

In the second part of the experimental studies, the hot gas from this burner, called vitiated air at Mach Number 1.67 is used for investigations on Z-D Supersonic Combustor. Static pressures are measured along the combustor wall for its performance evaluation. A comparison of wall pressure distribution in the axial direction through the complete length including burner, isolator for both hot and cold conditions are presented. In the hot condition, the burner

pressure is almost double compared to the cold flow situation and the difference in pressure distribution is clearly due to mixing and heat release in supersonic flow. The effect of equivalence ratio on wall pressure distribution is also studied and the results agreed well with the findings of other researchers (1,2).

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PERFORMANCE EVALUATION AND EXPERIMENTAL STUDIES ON METALLISED GEL PROPELLANTS

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Metallised gel propellants provide potential benefits for improving the performance of Chemical propulsion systems for future launch vehicles. They offer an increase in specific impulse, density and safety of rocket propulsion systems. The higher density of the propellant substantially reduces the tankage mass as well as the overall propulsion system dry mass. The other advantages are less vapourisation loss, no spillage or leak, reduced slosh problem and easy storage over the conventional liquid propellants. However, metallised gel propellants require design modification of flow system and prevention of nozzle erosion caused by higher temperature and solid particles in the combustion chamber. This paper presents the theoretical performance evaluation data and experimental results of studies conducted on metallised UDMH gel propellants.

A detailed performance analysis was carried out on metallised UDMH- N_2O_4 propellant system using metallic fuels-Al and Mg over a concentration range of 0-40% of the total fuel content and oxidiser-fuel ratios of 0.5 to 4.0. The performance parameters like I_{sp} , flame temperature and density-impulse were computed for wide range of chamber pressures and area ratios under equilibrium flow conditions. This analysis shows that metallised gel propellants deliver nearly 15-20 s of I_{sp} more and tankage fuel loading of 20 to 30% more than the non-metallised propellant. Aluminised UDMH gel propellant gives nearly 3 to 6 s higher I_{sp} than the magnesium gel propellant. Hence, Al is a better choice over Mg for metallised gel propellants. The peak vacuum I_{sp} values for 30% and 40% aluminised gel propellant are 316.7 and 318.7 s at O/F mixture ratios of 1.5 and 1 respectively under standard conditions. Thus, in the launch vehicle scenario, the direct substitution of metallised propellant over non-metallised liquid propellant would enhance the payload capability by 10 to 25%.

In this paper, studies on the development of metallised UDMH-gel propellant using pyrotechnic grade Al of 1.5 microns are presented. Handling and processing of superfine Al demand special precautionary measures. Parametric studies on the concentration of gellants, surfactants, superfine Al and process conditions are detailed. Gellant concentration could be drastically reduced by the use of superfine Al against propellant grade Al. The rheological characteristics of the gel propellants at different shear rates as also time dependency has been studied. The pseudoplastic and thixotropic behaviour of the gel propellant with superfine Al and propellant grade Al are compared. The flow behaviour of this gel propellant has been studied using a pressure vessel of 500 cc capacity using die holes of 0.75 to 2 mm under nitrogen gas pressure of 1 to 3 kg/cm².

BALLISTICALLY-MODIFIED PROPELLANTS

MECHANISM OF MODIFYING BALLISTIC PROPERTIES OF PROPELLANT FORMULATIONS BY **FAST-BURNING INCLUSIONS**

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The main goal of the present work is to develop a method of increasing the burning rate and decreasing the pressure exponent of different propellants when potentialities of catalysts have been exhausted or when they are ineffective at all; or when catalysts are not to be employed, lest the energetic performance or processing characteristics deteriorate. Adoption of fast-burning inclusions (FI) having the burning rates ten times greater than that of a base propellant has been suggested to solve this problem.

In this work, the binary compositions of main propellant components with fast-burning additives have been investigated. A combustion mechanism of such mixtures has been proposed that allowed a proper approach to regulate

ballistic parameters of propellants.

Studies on various compositions containing FI have been carried out in a constant pressure bomb in the pressure range of 0.1 - 40 MPa. Use of FI has shown an increase in the burning rate of composite formulations by several times even for formulation for which incorporation of catalysts is inefficient. Besides, some of FI are capable of decreasing the pressure exponent also up to negative values.

A combustion mechanism of propellants doped with FI has been proposed. Criteria for combustion stability and

controlling of modified propellants as well as criterion for efficiency of FI have been established.

EFFECT OF BURNING RATE MODIFIERS ON THE COMBUSTION EFFI-CIENCY OF COMPOSITE SOLID PROPELLANTS UNDER SUBATMOSPHERIC PRESSURES

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Better understanding of subatmospheric and low pressure combustion of solid propellant is necessary for the development of base-bleed propellant grains and stop-start solid motors, and for the accurate prediction of early stages of motor ignition transients. The composite solid propellant while burning at subatmospheric pressure is dominated by premixed flame. In missile base-bleed applications, the fuel-rich solid propellant grains are required to burn efficiently at subatmospheric pressures. Though composite solid propellants burn efficiently at low pressures below certain subatmospheric threshold pressure, the combustion efficiency drastically falls culminating in extinction at the pressure lower than this threshold pressure namely, the deflagration limit pressure. While extensive fuming of the propellant is a qualitative indication of this reduced combustion efficiency, the drastic reduction in the flame temperature should be the quantitative pointer. The present study investigates the effect of burning rate modifiers' (BRM) addition in unmetallized ammonium perchlorate (AP)/hydroxyl terminated polybutadiene (HTPB) composite propellants on this threshold pressure by the measurement of flame temperature using fine thermocouples. The BRMs used are copper chromite (CC) and ferric oxide.

Platinium-Platinum 10% Rhodium thermocouple wires of size 30 µm were welded together using argon arc welding technique. The bead diameters of the welded joints were measured using projection microscope and the thermocouples with a bead diameters of approximately less than 1.5 to 2 times the wire diameters were used. Propellants of mass composition AP:HTPB:Di-2-ethyl hexyl adipate:toluene diisocyanate = 73.00:21.60:4.05:1.35 were prepared. AP of weight mean diameter, (Σn_id_i⁴/Σn_id_i³), 98.5 μm was used in the propellant formulation and BRM equivalent to 2 per cent of the total mass of the propellant was added in the catalyzed formulation. Both the propellant formulations (uncatalyzed and catalyzed) were cast in a rectangular block of size 190 × 120 mm. Fourteen thermocouples were inserted at an angle of nearly 30° in two rows, 80 mm apart in the uncured propellant blocks and the blocks were then cured in an oven at a temperature of 80°C for four days. Propellant strands with inserted thermocouple wires were cut from the cured propellant blocks. To ensure uniform burning, the propellant strands were inhibited at their sides with a 10% polyvinyl alcohol solution. Nichrome ignition wire is inserted at one end of the strand. The strand is then fixed in a conventional bell jar set up (used for subatmospheric burning rate measurement) with provision to measure the flame temperature of a burning propellant strand. All the propellant strands were burnt under nitrogen atmosphere and the pressure was held constant in each case by continuously evacuating the bell jar. As the flame front of the burning propellant approaches and crosses the thermocouple, the millivolt signals generated by the thermocouple were amplified and continuously recorded in a PC/AT. Burning rates of the propellants at same pressure were determined separately using same bell jar set up. The recorded millivolts versus time signals were converted to the temperature—time or temperature—distance record through a computer code employing standard calibration equation and measured burning rate. The flame temperature of the propellant at a particular pressure was calculated by averaging the highest temperature recorded in the temperature-time record.

A typical temperature-time trace for 2% CC catalyzed propellant at various pressures shows a smooth rise in temperature till thermocouple arrives at the surface of the propellant. Thereafter, the temperature increases to final flame temperature with large fluctuations. The results of the study bring out that the flame temperature is essentially constant up to the threshold pressure and below this threshold pressure the flame temperature drastically falls showing significant reduction in combustion efficiency. It was also established that the threshold pressure is influenced by the addition of catalyst and the catalyzed propellant has lower threshold pressure.

EVALUATION OF FERROCENE DERIVATIVES AS BURN RATE MODIFIERS FOR AP-HTPB BASED COMPOSITE PROPELLANTS

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Composite propellants are used for military as well as space applications. Ammonium perchlorate (AP) based composite propellants consist of ferric oxide or copper chromite as burn rate catalysts. The use of ferrocene derivatives in the place of ferric oxide or copper chromite in these propellants is well reported. Ferrocene derivatives impart very high burn rates. These derivatives are also reported as plasticizers, crosslinking agents or bonding agents. Some of the ferrocene derivatives being liquid facilitate higher solids (AP/AI or both) loading, leading to better performance. However, use of ferrocene derivatives creates certain problems such as their migration to propellant surface and oxidation during storage.

Most of the information in this area is either patented or available in the classified reports. It was, therefore, decided to undertake the synthesis and characterisation of selected ferrocene derivatives which do not suffer from these shortcomings. Their performance was evaluated in composite propellants. Accordingly, four different ferrocene derivatives namely; 2,4 dinitrophenyl hydrazine derivative of monoacetyl ferrocene (solid), 1-pyrrolidinyl methyl ferrocene (solid), 1,1' di ter-butyl ferrocene (liquid) and 1,3 di-ferrocenyl-1-butene (liquid) have been synthesized and characterised for metal content, IR, NMR and HPLC.

In order to study the effect of their incorporation on performance, AP/HTPB based composite propellants containing these derivatives have been prepared by "slurry-cast technique" and evaluated for burn-rates, tensile strength, and % elongation. The propellant formulations were also subjected to static evaluation.

A comparison of properties of the propellants containing solid and liquid ferrocene derivatives has been done with propellant containing Fe₂O₃ and n-butyl ferrocene respectively. The data clearly brings out that the ferrocene derivatives studied during this work are superior to Fe₂O₃ and n-butyl ferrocene as well. The ferrocene derivative 1,3-diferrocenyl-1-butene (DFB) is the best among these derivatives and its production is being further scaled up in order to meet futuristic requirements.

ACTIVE COPPER OXIDE-AN EFFECTIVE BALLISTIC MODIFIER FOR SOLID PROPELLANTS

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The effect of various burn rate modifiers on ammonium perchlorate (AP) based solid propellants has been a subject of numerous investigations. Since the variation of burning rate directly affects the solid rocket performance prediction, considerable interest continues in the development of catalysts of reproducible performance and long range stability. In this paper, we present our studies on the synthesis of active copper oxide (ACO) and its evaluation as a reliable catalyst for AP based composite propellants.

A simple and efficient method has been developed for preparing highly active copper oxide in the laboratory. A number of laboratory scale samples were prepared and characterized by estimating the metal content, particle size, the acid sites and surface area. For this, X-ray powder diffractometry, SEM, particle size analysis, TPD and BET methods were employed.

To start with, experiments were done to determine the kinetic and catalytic activity of the prepared catalyst on the thermal decomposition of ammonium perchlorate. It was found that, unlike other transition metal oxides, copper oxide catalyses both the low temperature and the high temperature decompositions of AP. The efficiency of the catalyst was evaluated in HTPB propellant system containing AP/Al at a solid loading of 86%. Propellant charcteristics such as processability, mechanical properties, density etc. were determined. Burning rate was evaluated at 3 different pressures to compute the pressure index.

The burning rate was found to show consistent trends in all the three batches in six different evaluations. The efficiency was found to be slightly more than that of copper chromite. The ageing characteristics of the propellant with the new catalyst is being investigated on a long term basis. In addition to its simple synthetic route, this catalyst preparation offers low cost and good compatibility of the catalyst with other propellant ingredients and introduces no undesirable effect on rheological properties during propellant manufacture. It seems that this catalyst may be a potential ballistic modifier for solid propellants for future launch vehicles.

HIGH EXPLOSIVES

A REVIEW OF THE THERMAL DECOMPOSITION PATHWAYS IN RDX, HMX AND OTHER CLOSELY RELATED CYCLIC NITRAMINES

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Understanding the complex physicochemical processes that underlie the combustion and decomposition of energetic materials is essential to the development of reliable models for the performance, stability and hazard analysis of propellants and explosives and to provide a basis for improvement of ignition and sensitivity properties of their formulations. Since the nitramines RDX (I) and HMX (II) are important materials as propellants and explosives, we undertook over the years, a comprehensive, in-depth study of their thermal decomposition kinetics and mechanisms using unusual sophisticated techniques, namely, Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS), Time-of-flight velocity spectra analysis, Deuterium Kinetic Isotope Effects (DKIE), Isotope Labeling (15 N, 13 C and 18 O) and Isotope scrambling techniques. These studies are being extended to several less-known nitramines as well as to other newly synthesized, potentially important, candidate explosives.

In this invited paper the results obtained from condensed and gas phase decomposition studies of RDX and HMX will be reviewed in terms of reaction pathways (branches), bond-breaking and bond-forming steps, effects of phase on gas formation rates and rate controlling steps. A comparison will be made to the decomposition of four closely related cyclic nitramines, (III) to (VI) and the common modes of decomposition of nitramines will be highlighted. Briefly, the products of RDX decomposition were identified as H₂O, HCN, CO, CH₂O, NO, N₂O, NH₂CHO, NO₂, HONO, CH₃NHCHO, oxy-s-triazine (OST) and 1-nitroso-3, 5-dinitro-hexahydro-s-triazine (ONDNTA, III). Four primary reaction pathways control the decomposition of RDX in the liquid phase between 200 and 215°C. In the early stages of the decomposition of RDX in the solid phase, ONDNTA seems to be the only product which then leads to the formation of N₂O and CH₂O followed by other products associated with the liquid phase decomposition. These observations suggest that the decomposition of RDX occurs through formation of ONDNTA within the lattice. The latter was independently synthesized recently and its decomposition was shown to fit into the overall pattern of RDX decomposition.

HMX decomposes readily in solid phase above 235°C and yields: H₂O, HCN, CO, CH₂O, NO, N₂O, (CH₃)₂NNO, CH₃NHCHO, 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA) and a polyamide type nonvolatile residue. It too has several branches of reaction beginning with initial cleavage of an N-N bond which results in the unravelling of the ring. During this process, however, the N-N bonds are preserved appearing in one of the major products, N₂O. Some decomposition occurs in the lattice forming ONTNTA which goes on to decompose further. Deuterium kinetic

isotope effects suggest that water formed in the reaction probably acts as a catalyst in the decomposition. Quantitative measurements of reaction rates and isotope scrambling data will be presented in support of these broad conclusions with additional details of product formation from both RDX and HMX.

Research supported in part by the U. S. Army ARDEC, U.S. Army Research Office (ARO) and U. S. Department of Energy under contract No. DE-AC 0494AL 85000

DESIGN AND COMBUSTION BEHAVIOR OF EXPLOSIVE COORDINATION COMPOUNDS

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The combustion of coordination compounds (CC) of common formula [MLn]Am, where M is the central metal atom, L is ligand-fuel and A is anion such as perchlorate/nitrate is a subject of considerable interest because some of them have found specific application, in particular, as safe primary explosives or igniters.

To be capable of self-sustaining, burning CC should contain such molecular fragments that, themselves or their destruction products, possess oxidizing properties. These fragments are ClO₄, NO₃ and similar counter ions. A basis for designing such CC is making a choice of ligand which provides not only the fuel-oxidizer ratio and, consequently, heat of combustion, but also stability. In this paper, the main classes of organic compounds which might be used as ligands of explosive CC are discussed.

Burning rate of optimally designed CC depends mainly on two factors viz. nature of oxidizer and nature of metal. Change-over from nitrate ion to perchlorate ion usually raises the burning rate by a factor of 10 and more. Metal atom included in CC can serve not only as a matrix, which ties up ligand-fuel and anion-oxidizer, but also as a catalyst of redox reactions occurring during combustion. It was found during the present study that each anion-oxidizer has its own set of metals that possess a catalytic activity. Combustion mechanism of various explosive CC is proposed in this paper.

STUDIES ON ENERGETIC COMPOUNDS: RING-SUBSTITUTED ARYLAMMONIUM SALTS OF 3-NITRO-1,2,4-TRIAZOLE-5-ONE (NTO)

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3-Nitro-1, 2, 4-triazole-5-one (NTO) has been reported to be a potential member of a class of high energetic explosives(1) and offers attractive explosive performance with a high degree of insensitivity(2). A number of stable salts of NTO with basic compounds have been reported by many workers(3) which are moderately sensitive to impact and used as gun-propellant ingredients. As part of our ongoing programme to investigate energetic materials(4), we are reporting in this paper synthesis, characterisation and thermolysis of the ring-substituted arylammonium salts of NTO. Fifteen salts have been prepared by the interaction of aqueous NTO at 50-60°C with the solution of corresponding arylamine in 1:1 molar ratio as shown below:

$$NH_2$$
 + HN NH $50-60$ °C NH_3 N NH NO_2 NO_2 NTO $RSA NTOate$

where R = H, 2-CH₃, 3-CH₃, 4-CH₃, 2-Cl, 3-Cl, 4-CO₂H, 2-NO₂, 3-NO₂, 4-NO₂, 2-CH₃O, 3-CH₃O, 4-CH₃O, 2-C₂H₅O or 4-C₂H₅O.

All the salts were recrystallised from hot aqueous solution and characterised by TLC, TG, IR, pH and conductivity measurements. These studies have proved that all the salts are ionic in nature.

TG studies showed the removal of arylamine from each salt at >150°C, NTO is regenerated and decomposes at higher temperatures. NO₂ has been found to be evolved prior to ring rupture(5). The overall decomposition pathway of the RSANTOate can be summarised in the following scheme:

Proton transfer NH₂
$$\stackrel{}{\longrightarrow}$$
 NH $\stackrel{}{\longrightarrow}$ NH $\stackrel{}{\longrightarrow}$

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THERMAL DECOMPOSITION STUDIES OF A NEW GEM-DINITROALKYL NITRAMINE, 1,3,3-TRINITROAZETIDINE (TNAZ)

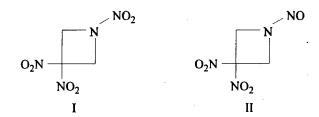
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1,3,3-Trinitroazetidine, commonly known as TNAZ(I), is a relatively new nitramine containing a four-membered ring and a gem-dinitroalkyl group. Since it is also a melt castable explosive with potential practical applications, study of its thermal stability and the degradation mechanisms are of interest particularly in comparison with the better known nitramines, RDX and HMX. Some such earlier studies have already been reported by Oyumi and Brill as well as by Lee et al.



This paper presents the results of a study of the thermal decomposition mechanisms of TNAZ using the simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS). The major products formed in the decomposition of TNAZ are NO₂ and NO with slightly lesser amounts of H₂O, HCN, CO/N₂, CO₂/N₂O and N-nitrosodinitroazetidine (NDNAZ, II). The last mentioned product, when independently synthesized and subjected to decomposition, also gave NO as a major product with lesser amounts of H₂O, HCN, CO/N₂ and CO₂/N₂O. The lower molecular weight products are similar to those observed in studies conducted previously by others. However, this study has shown that the mononitroso analogue of TNAZ, NDNAZ, has an important role as an intermediate in the decomposition of TNAZ.

The temporal behaviour of the ion signals associated with the various thermal decomposition products from TNAZ, TNAZ-1-15NO₂ and NDNAZ show the evolution sequence of the various products that are associated with the different reaction pathways which control the decomposition of these materials. In particular, the study of the 15N-labeled sample revealed that NO₂ originates from both the likely sites in the TNAZ molecule and that the cleavage of the N-NO₂ group precedes that of the C-NO₂ cleavage, resulting in similar sequences in the formation of NO and NDNAZ. At least five different reaction pathways in all, have been identified.

SYNTHESIS OF 4,4'-DIMETHYL-3, 3', 5,5'-TETRANITRO AZOXYBENZENE BY SELECTIVE REDUCTION OF TNT

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Triamino trinitro benzene (TATB), a thermally stable explosive can be synthesized by four routes starting from (i) 3, 5–D initrobenzoic acid (ii) TNT (iii) 1, 3, 5–Trichlorobenzene and (iv) 3, 5–Dinitroanisole. The synthesis of TATB from TNT by selective reduction has been patented. However, the formation of the title compound as a by-product has not been mentioned. Considering the availability of starting material and their cost, synthesis of TATB from TNT has been studied in detail. In this process, TNT is dissolved in dioxane and H₂S is passed for 3–4 hours in the presence of ammonium hydroxide which acts as a catalyst to selectively reduce NO₂ group at position 4 to –NH₂ group. The quantity of sulphur precipitated indicates the extent of conversion of –NO₂ group to –NH₂ group. After removal of sulphur, the reaction mixture is refluxed with KI/HCl for an hour, which yields a mixture containing 4–amino–2, 6–dinitrotoluene and 4,4'–dimethyl–3, 3', 5, 5'–tetranitroazoxybenzene as major constituents. The title compound has been characterized by IR, NMR and elemental analysis and has been assigned the following structure:

$$\begin{array}{c|c}
O_2N & NO_2 \\
H_3C & & CH_3 \\
O_2N & O & NO_2
\end{array}$$

Its thermal decomposition as well as explosive properties have also been studied. The data indicate that the title compound is stable upto 295°C and also safe towards impact and friction.

COMBUSTION OF ENDOTHERMIC POLYNITROGEN COMPOUNDS

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Combustion of endothermic polynitrogen compounds is of specific interest since the heat required for burning is evolved as a result of the primary decomposition reactions of endothermic fragments rather than of the secondary redox reactions, as in the case of nitro compounds. The main goal of the work is to elucidate how we can affect the burning rate of energetic materials by altering the chemical structure and reveal the reasons responsible for the burning rate level.

In the present paper, steady-state combustion of endothermic polynitrogen compounds such as nitroazidobenzene, tetrazoles and salts of hydrazoic acid with organic bases was studied in a window constant-pressure bomb over the pressure range of 0.1-40 MPa. The temperature profiles in the combustion wave were measured with 7 mm thick π -shaped tungsten-rhenium thermocouples.

When viewed as a whole, it emerges that in the case of energetic materials capable of combustion through decomposition of endothermic groups, it is the destruction process that controls the rate of burning. In this case, the chemical structure affects the burning velocity as it determines the rate of the decomposition.

INSENSITIVE EXPLOSIVES

AN ADVANCED BINDER FOR PLASTIC BONDED EXPLOSIVES

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Recent developments in the field of Plastic Bonded Explosives (PBX) necessitated the use of advanced polymeric binders versatile in properties and applications. At VSSC, a new polyol based prepolymer has been developed and successfully used as a binder in the formulation of PBX deployed in the destruct and separation system of flight rocket motors. This prepolymer is a product derived from indigenous polyol, reacted with diisocyanate under controlled reaction conditions. It is very cost-effective and has other advantages like ambient temperature curing, good pot life and processability.

The synthesis of the prepolymer involves drying of the basic polyol in a kettle for 2 to 4 hours at 80 to 100 °C under vacuum, followed by the addition of isocyanate at 40 to 60°C and continuing the reaction at 75 to 110°C under inert atmosphere for another 3 to 5 hours. When the free isocyanate content reaches 6 to 7%, the reaction is stopped and the product packed in nitrogen-blanketed glass containers. PBX is produced by incorporating RDX and dried castor oil in the above prepolymer and curing at about 60°C. The properties of PBX meet all the desired requirements and at present it is used in the destruct system of PSLV rockets.

DEVELOPMENT OF PLASTIC BONDED EXPLOSIVES : PRESSING STUDIES AND DETONIC PROPERTIES

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A new class of high energy materials known as Plastic Bonded Explosives (PBX) based on RDX and HMX in conjunction with various polymeric binder materials viz. Polystyrene, Polyvinyl acetate and Polyurethane have been developed. These energetic PBX compositions have been put under regular production from laboratory scale of 50 - 100 g/batch to pilot plant level of 3-5 kg/batch. The PBX moulding powder thus produced is then pressed using isostatic pressing technique. Various pressing parameters for the developed PBX moulding powder have been standardised to get optimum density of the pressed PBX charges.

Different properties viz. impact sensitivity, auto-ignition temperature, sensitivity to mechanical shock, F of I have been evaluated along with the density of the explosives. Other properties viz. velocity of detonation and detonation pressure have been determined using Ultra High Speed Photography Technique. VOD of the order of 8.4 mm/µs at a density of 1.72 g/cc has been attained as against that of 7.8 mm/µs for RDX/TNT 60:40 at 1.7 g/cc. These PBX compositions are practically useful for different types of explosive devices.

STUDIES ON PHYSICO-MECHANICAL AND EXPLOSIVE CHARACTERISTICS OF RDX/HMX-BASED CASTABLE PLASTIC BONDED EXPLOSIVES

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High mechanical properties, low vulnerability, high thermal stability in addition to high energy output are the need of the day for high explosive compositions to be used in future. Due to some major drawbacks associated with conventional high explosive compositions, the plastic bonded explosives (PBX) are emerging in a big way. The present paper describes the development of a nitramine/HTPB based castable PBX.

The PBX has been processed at 5 kg level by mixing the components in a planetary mixer for about three hours under vacuum at 50°C. The mix is then cast under vacuum at ambient temperature. The PBX has been made using bimodal/trimodal filler particles. Tap density experiments have been carried out with combination of the coarse and fine grades of explosive to establish the proportions required to give optimum packing in the PBX.

The optimum packing i.e. optimum density has been achieved with a bimodal mix of RDX as well as trimodal mix of HMX. By selecting the proper combination of explosive particle size, 88% solid explosive loading has been possible for making RDX/HTPB castable composition. Similarly HMX/HTPB compositions upto 88% of solid explosive loading were also possible. The impact and friction sensitivities have been determined by standard Fall hammer method and Julius Peter apparatus respectively. It has been found that a narrow particle size distribution reduces the impact sensitivity of the PBX. In general, the impact and friction sensitivity values are found to be lower than that obtained with the conventional cast explosive formulations.

The HTPB and DDI combination has been selected for their low viscosity as well as for ambient curing of the explosive charge. To attain a high solid loading while maintaining castability, the viscosity was required to be reduced further. This has been achieved by using DOA as plasticizer with binder/plasticizer ratio of 60/40 for optimum results. The processability of the binder system has been studied by using various wetting agents like lecithin, silicone oil and liquid paraffin. Silicone oil gave good results for achieving better processability. The same has been confirmed by viscosity profile of the various compositions. The processability was further improved by coating explosive particles with 2% DOA.

Bonding agents have been used to improve the interaction between the explosive particles and the binder. The tested bonding agents were TMP, pyrogallol, TEPAN and hexane triol. 0.3 to 0.5% of the TMP and pyrogallol gave about 50% increase in the compression strength of the PBX charge.

Thermal decomposition characteristics have been determined by using a micro DTA apparatus. The PBX composition is better in the sense that decomposition exotherm peak is obtained at 208°C whereas in conventional cast explosive composition, endotherm peak is seen at 80°C due to the phase change of the TNT.

For the measurement of VOD, the charge of the required dimensions was machined. VOD was measured by the probe method. The VOD of the compositions increases with the increase in the explosive loading. These values are found to be close to the theoretically estimated (BKW code) values for PBX of the similar explosive loading.

The results show that PBX can be manufactured with detonation properties better than Composition B with the added advantages of superior thermal and sensitivity characteristics.

BLAST WAVE INITIATION OF A SHEET EXPLOSIVE COVERED WITH METAL PLATES

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The study of initiation of detonation in explosives by a blast wave is of vital importance to avoid sympathetic detonation in various explosive stores and also to design magazines for safe storage of high explosives and ammunition. In the case of blast wave, the energy in the wave depends not only on pressure and time but also on the pressure profile of the wave. The pressure profile of a blast wave is not rectangular and its exact shape can be determined only by experiment. However, its peak over-pressure and duration are related through scaling law to reduced distance, $Z = R/W^{1/3}$, where W is the mass of the explosive which on detonation produces blast wave and R is the distance where blast parameters are measured. To the best of the authors' knowledge, no criterion for initiation of an explosive by a blast wave has so far been established. In this paper, an attempt has been made to establish such a criterion.

Initiation of an RDX-based sheet explosive by a normal incident blast has been studied during this work. The explosive sheet either bare or covered with different thicknesses of aluminium alloy metal plates were subjected to the blast wave. The intensity of the blast wave was varied by varying the distance between the sheet explosive and blasting charge. The values of critical distances obtained, in the case of sandwiched sheet explosives, have been fitted to an exponential curve:

$$R = AW^{1/3}e^{-(B/W^{1/3})\cdot X}$$

where 'R' denotes the distance between the sandwich and the donor charge and 'X' represents the thickness of the plates in metres, 'W' is the mass of the donor charge in kg, 'A' and 'B' are the constants. The values of these constants have been obtained as A = 0.2133 and B= 48.2 for the donor charges weighing from 100-600 g and the covering plate of thickness varying from 4-12 mm.

In the case of bare and foil-wrapped sheet explosives, the values of critical distance R₀ are fitted to an equation

$$R_0 = A_0 W^{1/3} e^{(B_0 W^N)}$$

where A_0 , B_0 and N are constants.

For bare sheet, the values of the constants A₀, B₀ and N are 0.153, 1.285 and 1.632 respectively. In the case of foil-wrapped sheet explosives, the corresponding values are 0.215, 2.690 and 3.437 respectively. It has been observed that higher the thickness of the metal plates, higher is the incident pressure required to initiate the sheet explosive. Interestingly, if the sheet is covered by only a thin aluminium foil of 0.25 mm thickness, then the critical pressure required for its initiation is smaller than that required for initiating a bare or metal covered sheet. The experimental values of initiating pressure obtained for different plate thicknesses and different quantities of donor charges have been fitted to a relation

$$P = A e^{(B/W^{1/3}) \cdot x}$$

where P, x and W represent pressure, thickness of the plate and mass of the donor charge. If pressure, thickness and charge quantity are expressed in kg/cm^2 , m and kg respectively,then the values of constants are A = 179, B = 47.8 for 0.1 kg and A = 155, B = 54.1 for 0.4 kg and A = 151, B = 54.1 for 0.6 kg of donor charges. The variations in critical pressure with quantity of donor charge for initiation of bare and foil-covered sheet explosive,

however, follow the relation

$$P = A_0 e^{B_0 \cdot W^N}$$

where $A_0 = 226$, $B_0 = -1.78$ and N = 1.67 for bare sheet explosive and $A_0 = -13.889$, $B_0 = -13.89$ and N = 5.56 for foil-wrapped sheet explosive. It has also been observed that initiation of the sheet explosive by a blast wave occurs after a delay of about 2 μ s when it is covered with thin aluminium metal foil and about 7 μ s when it is covered with 4 mm thick aluminium metal plates.

EXPLOSIVES - INITIATION AND POWER

IGNITION OF EXPLOSIVES BY A HEATED WIRE

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The knowledge of the ignition parameters of high explosives (HE) is of definite scientific interest for both developing the ignition kinetics models and assessment of their hazards. The present investigation was undertaken to determine ignition temperature of model explosives of high density based on HMX and TATB by applying the technique of firing ballistic powders by heated wire as opposed to known techniques for the HE ignition temperature determination (1). The authors investigated the HE ignition temperature depending on the time and rate of heating. The technique makes it possible to calculate heat pulses and heat flows leading to ignition.

On decreasing the heat flow, the time for the HE heating up to ignition increases and ignition temperature falls, thereby approaching the critical value characterizing the danger limit under accidents associated with heating.

The ignition of HE based on HMX and TATB takes place in a different manner. With the explosive material (EM) based on HMX during great heat flows the ignition beginning from the surface in the form of "firing" is typical but when achieving the critical parameters the heated layer flash takes place which increases the probability of the explosion realization. EM based on TATB always ignite in the form of "firing" independent of the heat flow that points to the higher extent of its safety. The data obtained correlate well with the other parameters of ignition.

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COMPARATIVE ASSESSMENT OF THE EXPLOSION POWER UNDER THE THERMAL AND SHOCK-WAVE INITIATION OF EXPLOSIVES

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The heating of high explosives (HE) contained in the closed volume of the shell leads to the thermal explosion. The intensity of the similar explosion is difficult to predict and depends on many factors which impede the modelling of this process when performing experiments and calculations. In this connection, the authors have undertaken the investigations in which the HE sample of high density has been initiated by a weak shock wave in a set-up simulating the thermal explosion. Under the shock-wave initiation, the HE explosive transformation has given the same kinetic effect as in the case of thermal explosion.

The kinetic effect of the explosion has been estimated according to the relative throwing capability by measuring the flight velocity of the thrown plate (1). In this work, the plate acceleration velocities under thermal explosion and the data obtained under the shock-wave initiation of the explosion is compared in the form of the dependence W = F(X) (2).

In these experiments, the measurements of the initiating shock wave parameters, namely, the amplitudes of incoming/outgoing waves (by manganine dandes) and the average rate of the explosion process in the sample (by electrocontact dandes) have been carried out. Thus, the authors believe that for the purpose of the explosive transformation power modelling under the thermal initiation it can be substituted in the experimental investigation by the process developing in HE as a result of the action of the shock wave with known parameters.

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INVESTIGATION OF THE PROCESS OF DEFLAGRATION-TO-DETONATION TRANSITION (DDT) IN GRANULAR SECONDARY EXPLOSIVES WITH HIGH SPEED PHOTOGRAPHY

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The process of deflagration-to-detonation transition (DDT) in granular secondary explosives has been investigated with high-speed photography. It is generally understood that the ultimate stage of the DDT process is the shock initiation of detonation. Information about the formation of this final critical shock has been obtained through high-speed photography by thermally igniting charges of confined secondary explosive.

Studies were carried out on the secondary explosives: 1-(5-cyanotetrazolato) pentamine cobalt (III) perchlorate (CP) and pentaerythritol tetranitrate (PETN). These two materials have shock initiation pressures which are relatively low compared to most other secondary explosives. This property makes them ideal for use in a study which requires transparency in the confinement for photography and consequently, a reduction in the strength of the confinement.

The study has highlighted the importance of compaction in the acceleration of the reaction front to the point of DDT. The previously considered importance of convective burning from ignition to DDT has been shown to be important only in the initial rapid increase in pressure immediately following ignition.

The results are important in the design of a non-primary electrical detonator, in the avoidance of DDT in burning propellants and in accidental deflagration scenarios. The numerical modelling of the DDT process will also be improved from the experimental observations.

DYNAMIC MEASUREMENTS OF INITIATING OUTPUT OF EBW DETONATORS

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In modern warfare, any ammunition must function accurately and reliably. It must be safe in storage, handling and use under stringent conditions. The initiation output of any device can be considered from two aspects, one being the functioning of the device, the other is potential for unintentional initiation from safety aspects. The main explosive filling of the device must not be prone to accidental initiation. To achieve this, explosive compositions are chosen which are relatively insensitive but have large energy outputs. Compounds are known which are readily initiated by relatively small energy inputs (lead azide etc) but in general, they have fairly low energy outputs. Moreover, it would be unsafe to use large quantities of sensitive compositions to have more outputs. Mostly, booster is used between the two extremes to have the required outputs due to transfer of detonation wave.

The initiation of the booster and main charge of a detonation train occurs by the action of the detonation shock-wave produced by the components or device as it detonates. If this shock wave at great pressure leaves one charge (donor) and impinges directly on another (acceptor), then at first the pressure will drop as the decomposition occurs and then it will rise to stable detonation. Now if the device is closed, the pressure will reduce before entering the acceptor interposing a barrier, then acceptor may or may not initiate depending on the output of the donor devices, thickness of the barrier and also the ease of initiation of acceptor.

A special electro-explosive device, which is based on exploding bridge wire phenomenon has been designed and developed, known as Exploding Bridge Wire (EBW) Detonator. This device is safe and reliable as only secondary high explosive is being used in it. Deviation from uniformity, due to human error on engineering deviation in the fabrication process of detonators can cause enough variation in the details of energy transfer to effect initiation of explosive trains. For optimisation of the design of exploding bridge wire detonators and reliable initiation of explosive train, the experiments were carried out to assess the overall initiating output of the detonators.

The output of EBW detonators was checked by means of dent test. The output is indicated by the depth of the dent produced in the 5-10 mm thick mild steel and an aluminium plate. The volume of dent or cavity is measured and compared with that obtained using conventional detonator No.33. However, dent test is an end result in which variation of output with time cannot be deduced. Thereby, quantitative dynamic output with time cannot be deduced by applying this test. Quantitative dynamic measurements of output is carried out by using ultra speed cameras like Streak Camera, Framing camera and Flash Radiography. During this work, underwater pressure, pressure in air, barrier thickness or the thickness of bulk-head from safe arm mechanism and shock pressure etc were calculated. The effects of electrical energy on output of detonators were also calculated from safety point of view. The detonators were subjected to environmental tests like vibration, thermal cycle, bump test and their performance output evaluated.

It was observed that gaps between bridge wire and low density explosive, high density column of explosive have bearing on the time of initiation and delay. The 4-5 mm Aluminium barrier can be used as bulk head barrier in Safe and Arm design. PBX, CE and RDX/TNT charge are initiated directly by the EBW Detonator.

STUDY OF FLYER PLATE IMPACT ON A TARGET

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The flyer plate impact on a solid target is often used for generation of high pressure shock wave for determining equation of state of solids at such high pressures which are not attained by static methods. In addition to this, the flyer plate impact on a solid also produces indentation on the impacted surface and scabbing on its free surface. These aspects of flyer plate impact are considered important for many military applications.

In this paper, an attempt has been made to study theoretically various aspects of flyer plate impact in general and the phenomenon of indentaion and scabbing in particular. It has been assumed in this study that the target and the flyer plate are made up of the same material and the impact of the plate causes one-dimensional flow of the material. Considering the material to be compressible, the relations for the pressure and particle velocity in the non-uniform shock wave, indentation on the impacted face, maximum width of the rectangular pressure profile, critical thickness of the target where attenuation of the shock pressure commences, minimum thickness of the target which is sufficient to avoid scabbing and the thickness of the scab produced by the non-uniform shock wave have been derived. In order to derive these relations the pressure and particle velocity profile of the shock wave in the target, and the attenuation of its peak pressure with distance travelled have been determined. Analysis has also facilitated the determination of pressure profile of the shock wave at different locations in the target.

The results obtained show that the pressure profile of the shock wave is approximately triangular, the thickness of the scab and depth of indentation are dependent on the thickness of the flyer plate, the target and the impact velocity of the flyer plate. The attenuation of the peak pressure of shock wave generated by the flyer plate of thicknesses 1, 3 and 6 mm impacting the target with velocities of 0.4, 0.6 and 0.8 mm/ μ s has been found to follow a curve,

$$P = P_0 \cdot e^{-\alpha \cdot \Delta x}$$

where α is the constant of attenuation, P_0 is the unattenuated shock pressure, Δx is the distance from the point of start of pressure attenuation in the target. In order to verify the correctness of the present analytical approach, the calculations have been repeated for impact of aluminium flyer plate on aluminium target and attenuation of shock pressure with distance obtained here, has been compared with similar results presented by Fowles. It is seen that the present results are in good agreement with those of Fowles obtained by different numerical analysis.

ENERGETIC POLYMERS AND OXIDIZERS

THE COMBUSTION AND COMBUSTION INSTABILITY CHARACTERISTICS OF ENERGETIC AZIDE POLYMERS

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To understand the mechanisms of solid propellant combustion, it is important to understand the fundamental mechanisms involved in the combustion of monopropellants. This paper will focus on the combustion characteristics of solid monopropellants which contain the azide bond, such as GAP, BAMO, AMMO etc. Data from several literature sources have been compiled and will be used for comparison. The basic decomposition characteristics will be reviewed, summarizing their relationship to combustion characteristics. The basic combustion characteristics, such as burning rate, surface temperature, surface heat release, temperature sensitivity will be reviewed and compared for various azide polymers and related to oscillatory characteristics. Data compiled from several literature sources will be used for comparison with the fundamental flame modelling approach to combustion instability normally used in the US.

Emphasis will be placed on examining the physical mechanisms that have a direct influence on either the magnitude of the burning rate or on the unstable response. Particularly the relationship between the surface heat release, the temperature sensitivity and the unstable response will be examined for different azide containing ingredients and parametrically from a modelling point of view. These properties relate directly to the B parameter in the US flame modelling approach and to the k parameter in the ZN approach. This relationship will also be examined. Calculated response values for ingredients will be presented showing the anticipated values that have not been measured experimentally.

A fundamental steady state model based on detailed flame kinetics has recently been developed by BYU, based on the pioneering work of Melius, Yetter, and others. The model has previously been applied to RDX and HMX. Comparisons between those modelling calculations and available experimental data, are in reasonable agreement for burning rates, temperature profiles, major species and most minor species. Preliminary calculations of the model have been made for GAP, and those results are presented in this paper. The calculations show the burning rate and temperature profile through both the solid and the gas, and the profiles of the combustion species, both in the reacting condensed phase and the gas phase.

SYNTHESIS AND CHARACTERIZATION OF HYDROXY TERMINATED POLYEPICHLOROHYDRIN AND POLYGLYCIDYLAZIDE

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Polyglycidyl azides with molecular weight more than 2000 and 1,00,000 have been synthesized by reacting polyepichlorohydrin (PECH) diol with sodium azide in dimethyl sulphoxide. The conversion of the chloropolymers to azide polymers was above 90% as estimated by fast neutron activation analysis. PECH of \overline{M} n around 2000 was synthesized by activated monomer polymerization of epichlorohydrin using boron trifluoride-ethylene glycol complex as catalyst while aluminium triethyl-ethylene glycol complex was employed as catalyst to get PECH of \overline{M} n more than 1.00.000. The polymers were characterized by various spectral analysis, fast neutron activation analysis and molecular weight measurement. The PECH diols and their corresponding azides of \overline{M} n greater than 2000 and 1,00,000 cured readily with toluene diisocyanate using triethylamine and dibutyl tin dilaurate as catalysts.

FAST NEUTRON ACTIVATION ANALYSIS OF HIGH ENERGY MATERIALS AND POLYMERS

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Fast neutron activation analysis (FNAA) technique using 14 MeV neutrons has been applied to estimate nitrogen, chlorine, oxygen and aluminium in explosives and propellants. FNAA also has been employed to determine nitrogen, oxygen, chlorine and fluorine in various polymers. The technique is fast, accurate, non-destructive and non-hazardous in analysing elements in explosives and propellants compared to a number of chemical methods which are time-consuming, less accurate, suitable for single elemental analysis and do not measure oxygen directly. In this paper, FNAA technique, its theory and application for estimation of elements in high energy materials carried out in the laboratories of the authors have been reviewed. The method also helped to determine the differential distribution of aluminium and ammonium perchlorate in aluminized explosives and rocket propellants. Modification of polyepichlorohydrin to polyglycidylazide was followed by FNAA more accurately than IR spectral analysis.

POLYMERS AS BINDERS AND INHIBITORS

MODELLING OF POLYURETHANES BASED ON HYDROXY TERMINATED POLYBUTADIENE: PREDICTION OF MECHANICAL PROPERTIES OF SOLID PROPELLANTS

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Forty formulations based on four different grades of hydroxy terminated polybutadiene (hydroxyl value 20 - 40 mg KOH/g) at r = [NCO]/OH] value in the range 0.7 - 1.0 with varying amounts of trimethylol propane/butane diol and containing 86% solid loading were consdered to test the applicability of the α -model of Marsh et al for the prediction of the mechanical properties of composite solid propellants. Two network parameters, crosslink density (Ve) and effective chain length (LX), were calculated from the model. Tensile strength and modulus were correlated to Ve and elongation at break to LX. Using the correlations obtained from experimental data at r = 0.8, mechanical properties of the various formulations were predicted. Good agreement between experimental and predicted properties was obtained for formulations with modulus > 100 N/cm2. Probable reasons for deviation observed at r < 0.8 and low modulus values are discussed. Improved correlations between mechanical properties and network parameters, applicable over a wide range of formulations were arrived at. The standard errors of prediction were found to be close to ± 1 σ value of the measurement.

HTPB-BASED TRIBLOCKS AS ADDITIVES IN COMPOSITE PROPELLANTS

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Hydroxyl terminated polybutadiene (HTPB) is one of the most important polymeric fuel binder for composite propellants (1). In this work, we utilised the hydroxyl functional group of HTPB to anchor tungsten hexachloride (2,3). This anchored catalyst was able to polymerise various monomers like phenyl acetylene, norbornene and norbornadiene via metathesis polymerisation (4). The triblock copolymers thus obtained are of the type A-B-A and have been characterised by IR. 1 H/ 13 C NMR, TGA, DSC etc.

These triblock copolymers based on HTPB were employed as additives to solid propellant mixture with ammonium perchlorate (oxidiser), dioctyl adipate (plasticizer) and toluene diisocyanate (curing agent). Burning rate studies of these propellant mixtures were conducted under various pressures to evaluate the ballistic nature. It was found that phenyl acetylene and norbornene based additives impart higher burning rate than the corresponding HTPB based propellants. This paper mainly discusses the synthesis, characterisation and burning rate studies of the above triblock copolymers.

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STUDIES ON POLYURETHANE-BASED INHIBITION FOR HIGH FLAME TEMPERATURE COMPOSITE DOUBLE BASE PROPELLANT

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Propellant technologists desire a definite pattern of propellant burning for speicific applications which is achieved by restricting propellant burning using inert polymeric materials called inhibitors. Although, a large number of inhibition systems are reported for double base and composite propellants, literature available on inhibition of composite double base propellants (Composite DB) is limited.

Inhibition systems based on epoxy resin and butadiene-acrylic acid copolymer have been reported in literature for composite DB propellants. Styrene-butadiene or acrylonitrile-butadiene rubber blended with PVC or ethylene-propylene copolymer, glycidyl acrylates/glycidyl ether have also been suggested as inhibitor for this class of propellants. PVC-based systems are known to undergo deterioration due to dechlorination while epoxy binder poses post-curing problems leading to brittleness. In general, polymers with ester linkage are relatively more prone to hydrolysis. Moreover, slurry cast composite DB propellants are more flexible than conventional double base propellants. This results in stresses at propellant-inhibitor interface during thermal cycling if there is a large difference in mechanical properties of propellant and inhibitor. Another major challenge posed by composite DB propellants is their higher flame temperature than DB and composite propellants due to AP-Al combination and nitramines dispersed in energetic double base matrix.

In view of this, a research programme was undertaken to develop thermally resistant, flexible inhibition systems based on polypropylene glycol (PPG), hydroxy terminated polybutadiene (HTPB) and their combinations. During the initial work, polymer sheets were prepared by slurry cast technique. TDI was used as a curative and pyrogallol was added as crosslinker-cum-antioxidant. Lithopone was used as a filler. Crosslinking catalysts, dibutyl tin dilaurate (DBTL) and ferric acetyl acetonate (FeAA) were used for PPG and HTPB based systems respectively. Mechanical properties of the sheets were determined by using Instron Universal Material testing machine.

PPG based composition was found to be highly flexible with low tensile strength (40 - 66 N/cm²). In order to improve upon the structural integrity, PPG, which has high flexibility due to presence of C-O-C bond in the backbone, was incrementally replaced by HTPB. Polymeric sheet obtained with HTPB binder system gave T.S. of 100–120 N/cm². Effect of curatives and fillers on processability and mechanical properties was also evaluated. During this study, isophorone di-isocyanate (IPDI) was found to be superior to toluene-di-isocyanate (TDI) and diphenyl methane di-isocyanate (DDI) in view of reasonable pot-life as determined by monitoring viscosity profile. Among various fillers, a combination of antimony trioxide (Sb₂O₃) and carbon black (C-black) gave superior reinforcement as revealed by high T.S. of the composition (140 - 160 N/cm²). On the basis of these findings HTPB-IDP-IPDI based formulation was further studied for its thermal behaviour and plasticizer migration.

Subsequently, a technology was established to apply the optimised polymer composition as inhibition system to nitramine based slurry cast composite DB propellants. An effective bonding between the propellant and the inhibitor was established by determining peel-off and bond strength. In order to get realistic data from application point of view, inhibited propellant sets were subjected to static evaluation at ambient as well as extreme temperatures (-30°C and +55°C) in cigarette burning mode. A smooth P-t profile was obtained during the combustion of propellant grains, thereby establishing the practical utility of the composition developed. The data was also generated on slurry cast AP–Al composite/composite DB propellant as well as extruded composite DB propellants.

SYNTHESIS AND CHARACTERIZATION OF COPOLYURETHANES BASED ON HYDROXY TERMINATED POLYBUTADIENE AND ITS HYDROGENATED ANALOG

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The tailoring of the mechanical properties of composite solid propellants is often resorted to suit various mission requirements. In this communication, the use of copolyurethanes involving HTPB and its hydrogenated analog (HHTPB) to achieve propellant grains with wide ranging ultimate properties in a more controlled manner is reported. The presence of sp³-sp² carbon-carbon single bonds in HHTPB compared to sp³-sp³ single bonds in HTPB, imparts greater stiffness to HHTPB-based urethane networks and enhance the mechanical strength of the copolyurethanes. Further, since the functionality distributions of HTPB and HHTPB are nearly the same, addition of HHTPB results in enhancement of properties, such as tensile strength and modulus at nearly the same elongation values. Thus, urethane networks having similar modulus and tensile strength with widely varying elongation values and vice versa were synthesized by altering the comonomer ratio and the stoichiometric ratio (NCO/OH). The properties obtained are in conformity with the expected trends.

Further, the urethane networks were characterized by dynamic mechanical studies and the loss tangent (tan δ) storage (E1) and loss (E2) moduli were determined at various temperatures. Arrhenius plots were obtained relating log E1 and log E2 with temperature. The activation energy (16 kJ/mole) determined by the storage modulus data has been found to match with the C-C bond rotational barrier, while the value (35 kJ/mole) determined by the loss modulus data matches with that of the viscous flow. Solid propellants based on these copolyurethanes have been made and characterized for their mechanical strength and burn rates. The effect of copolyurethane composition on the mechanical properties of the solid propellants also follow the similar trend as in the case of gum stocks. However, the burn rates are not found to be dependent on the composition of the copolyurethanes.

PYROTECHNIC DEVICES

THERMAL STUDIES ON A BORON-BASED INITIATOR FORMULATION

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Boron-potassium nitrate combination is a well known pyrotechnic formulation that finds extensive applications in Space ordnance. It is possible to convert this versatile composition into a hot-wire sensitive 1A/IW initiator formulation, which can find application in launch vehicles by adding an additional fuel, lead thiocyanate. The paper deals with the ignition behaviour of this tricomponent system vis-a-vis the bicomponent ones. The parameters studied include ignition temperature as a function of thiocyanate percentage, ignition delay as a function of temperature, kinetic parameters based on DSC studies and these values were compared with those of boron-potassium nitrate. The ignition temperature is found to decrease as the percentage of thiocyanate is increased and the plot follows almost a binomial fit with the initial portion being linear. The kinetic parameters like activation energy and Arrhenius pre-exponential factor have been computed using Kissinger's method and also by determining the ignition delay in isothermal runs. From these values, it could be confirmed that in squib formulation, the rate determining step is the reaction between lead thiocyanate and potassium nitrate. This is followed by the more energetic reaction between boron and potassium nitrate. By suitably adjusting the percentage of the three ingredients, it is possible to obtain a suitable ignition temperature for the charge so as to conform to the requirements of a 1A/IW initiator formulation.

DEVELOPMENT OF ZIRCONIUM-POTASSIUM PERCHLORATE INITIATOR FOR SPACE APPLICATIONS

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Zirconium-potassium perchlorate is found to be a very promising composition for initiator application. The paper deals with the work carried out for developing an initiator based on this formulation and the tests done on both the charge and the initiator. Since the number of ingredients is only two and their average particle size as well as proportions are nearer, mixture homogeneity is easily attained in this formulation leading to better consistency in its functional characteristics. It has got an ignition temperature of about 490°C, which is comparable to that of the existing boron-based formulation. However, it has got a lower specific heat which brings down the ignition energy requirement as well as ignition delay, and the flash always precedes bridge wire fuse. Further, the higher solid content in the reaction products ensures better heat transfer to and initiation of the next element in the train. Preliminary tests based on Bruceton analysis have been carried out and the electrical characteristics estimated which are found to satisfy the requirements of a 1A/1W initiator.

EFFECT OF FUEL CONTENT AND PARTICLE SIZE DISTRIBUTION OF OXIDISER ON THE IGNITION CHARACTERISTICS OF METAL-BASED PYROTECHNIC COMPOSITIONS

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A systematic study has been carried out to evaluate ignition behaviour of boron-based pyrotechnic compositions by varying the boron content from 5 to 50% while keeping binder percentage constant and by varying particle size distribution of KNO₃ from 53–90 micron to 53–600 micron in magnesium-based pyrotechnic compositions. The data have been generated on calorimetric value, packing density, ignition temperature, friction and impact sensitivity, ignition delay, pressure maximum and time to reach pressure maximum.

In the first set of study on boron based pyrotechnic compositions, the calorimetric results indicate that compositions with 20% boron give maximum exothermicity. On further increase in boron content, decrease in cal val resulted. It was seen from friction sensitivity tests that all compositions were insensitive up to 36 kg dead load. It was further observed that all compositions are insensitive to spark up to 5 Joules of energy. However, compositions having boron content 30% and above were found to be relatively less sensitive to impact as against compositions with less than 30% boron.

The minimum ignition temperature of 502°C was obtained for 30% boron composition from DTA. However, an increse in ignition temperature was observed on further increase or decrease in boron content.

From the closed vessel data it was noticed that pressure maximum (P_{max}) initially increased with increase in boron content and at 20% boron content, P_{max} recorded was the highest. However, on further increase in boron, the P_{max} went on decreasing. The ignition delay reduced with increase in boron content and attained minimum value for 30% boron and remained constant for subsequent increase in boron content. The time to reach pressure maximum decreased with increase in boron content up to 30% and remained at almost constant level with further increase in boron content.

Amongst the compositions studied, those containing 20, 25 and 30% boron seemed to be attractive igniter compositions. However, from handling, storage and processability points of view, the composition with 30% boron is found to be superior as compared to 20 and 25% boron-based compositions. In addition to this, minimum value of ignition temperature, ignition delay and optimum mass consumption rate make the composition with 30% boron superior to those with 20 and 25% boron.

In the second set of experiments, a study was undertaken to investigate the influence of oxidizer particle size distribution on the ignition efficiency of a magnesium-based pyrotechnic composition. The potassium nitrate (KNO₃) in four particle size distribution ranges viz. 53–90 micron, 53–150 micron, 53–300 micron and 53–600 -micron were selected. The results obtained indicated a progressive trend in ignition temperature and ignition delay while going from wider particle size distribution viz. 53–600 micron to narrower particle size range viz.53–90 micron of KNO₃.

The ignition delay of 0.065 s for 53–600 micron increased nearly four times (0.2345 s) for 53–90 micron and the ignition temperature which was 572°C for 53–600 micron increased to 616°C for 53–90 micron. However, the packing densities were found to decrease gradually from 1.25 g/cc for KNO₃ of 53–600 micron to 0.93 g/cc for that of 53–90 micron. The pressure maximum and cal val remained in the same order for these compositions.

A correlation between packing density, ignition temperature and ignition delay was established. The increase in packing density (leading to better intimacy of the solid reactants) and lowering of ignition temperature and ignition delay of a magnesium-based pyrotechnic composition were observed with wider particle size distribution of the oxidizer. The results can be explained on the basis of "Apollonian Triangles". A further attempt has also been made to interpret the findings by using geometrical distribution of particle sizes of oxidizer and fuel.

BURSTING SMOKE AS AN INFRA-RED COUNTERMEASURE

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Smokes have been used in Defence for a large number of applications like screening, blanket ground installations from aircraft observation, creating dummy screens, training, simulating battlefield scenario and as a countermeasure to high technology weapons using infra-red sensors/guidance systems. Smokes can be created by condensation of vaporised material, dispersion of solid/liquid and explosive dissemination of finely powdered material using explosive energy in the form of bursting charge (termed as bursting smoke). These bursting smokes produce large sized particles almost instantaneously and hence hold promise as an infra-red countermeasure.

As the major information on use of bursting smoke as a countermeasure to IR sensors is in the form of patents and very limited information is available in the open literature, in the present investigation, a number of bursting type of smokes (using various powders like bronze copper lined flakes, bronze flakes, graphite, carbon black, dolomite, french chalk and chaff) and a central high explosive charge were evaluated for attenuation of IR in the 8-13 µm band using SR 5000 spectroradiometer.

The particle size and shape were determined microscopically using Carl Zeiss Jena Neophot-21. The particle size of powder as determined were 10 μ m (bronze copper lined flake), 3-10 μ m (bronze flake), 2-6 μ m (graphite), 0.1 - 1 μ m (carbon black), 10 μ m (dolomite), 1-5 μ m (french chalk) and 15.5 mm length (chaff). These powders were individually hand-tapped in cylindrical tin containers (vol. 900 cc) having a central aluminium tube with 7 g of plastic explosive. Each container was placed between a source of IR radiation (hot plate) and SR 5000 spectroradiometer (M/s.RMP France) separated by 70 m distance and the powder was dispersed using electric detonator No.108. Cadmium mercury telluride (CMT) detector cooled by liquid nitrogen was used.

The results obtained indicate that bronze copper lined flakes, bronze flakes and dolomite produced average attenuation between 93 and 100%. The duration was around 13 s in case of flakes, while it was only 5.5 s for dolomite. Graphite powder gave 88–100% average attenuation for a duration of 11 s, while carbon black produced only 58–100% attenuation for the same period. French chalk produced 85–100% average attenuation for a duration of 5 s. Mixture of bronze flake and chaff gave attenuation 97–100% for around 12 s, while mixture of bronze copper lined flakes, bronze flakes and chaff produced similar attenuation for about 8 s. The highest attenuation of 8–13 µm radiation was produced by a mixture of chaff with bronze flakes and the mixture of chaff with bronze copper lined flakes and bronze flakes. Alone, bronze flakes or bronze copper lined flakes or dolomite powder gave lower attenuation than the chaff mixture, but higher than graphite powder. French chalk powder produced lower attenuation than graphite while least attenuation was produced by carbon black.

The IR attenuation is produced due to physical blocking of IR radiation by particulate material. Larger the size of particles of the flakes, more is the attenuation produced. In the case of bronze copper lined flakes, bronze flakes and mixture of flakes with chaff, higher attenuation and higher duration (as compared to other powders) may be because of larger size and floating of material in the air to physically block the IR radiation, in view of its flaky nature.

IGNITION TRANSIENT

HEAT TRANSFER AND IGNITION OF A VISCOUS LIQUID PROPELLANT IN THE CHANNEL

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It is well known that the heat transfer at channel wall determines in many respects the chemical reaction mode in the flow. If the intensity of heat removal is high enough, chemical reaction proceeds in a low-temperature mode characterized by insignificant changes in reagent temperature and its concentration. If the intensity of heat release in the flow exceeds the intensity of heat removal, chemical reaction may occur in a high-temperature (explosive) mode. The latter is inadmissible in practical systems, so the need has appeared to investigate the heat transfer characteristics and the conditions for ignition in a flow.

We will be dealing with the heat and mass transfer as well as flow parameters for a high-viscosity liquid in a cooled channel with the reaction proceeding in a low-temperature mode. This mode is characterized by a weak effect of the heat release due to chemical reaction on the heat balance in the flow. For high initial temperatures, one can clearly distinguish the boundary layer region and the flow core where the liquid velocity is nearly the same throughout. Downstream of the channel inlet, owing to the presence of friction, the flow velocity near the wall decreases and increases in the core of stream until the boundary layer arrives at the channel axis. As the liquid temperature decreases, the viscosity increases and even three characteristic zones can be distinguished in the channel. One of them is the boundary layer region immediately adjoining the channel wall. Next is high-viscosity liquid flow region (with high viscosity caused by the cooling of the flow at the wall) where the thickened liquid moves as a solid body. Finally, the high-temperature low-viscosity liquid flow region is observed, which is characterized by a parabolic axial velocity distribution. The formation of the axial profile far downstream of the inlet is mainly governed by the flow rate. When inlet axial velocity is low, the liquid will thicken due to heat removal and adhere to the walls of the channel. In this case, the flow pattern resembles the flow in a diffuser. On the contrary, characteristics of the high-velocity flows result in the heat release in the near-wall region. The increase in temperature in the peripheral regions of the flow results in a decrease in viscosity and the comparatively "solid" bulk of thickened material is sliding along the walls of the channel.

The most interesting results are observed at low values of inlet temperature of the liquid. In this case, the dissipation of the mechanical energy is so intense that the flowing liquid is heated to high temperatures in the peripheral region. The calculation performed shows that the heat released in the flow due to friction may affect substantially the heat transfer at the wall. When the flow velocity is high, a state may set-in where the heating of the flow by friction forces may accelerate the chemical reaction and change it from the low-temperature mode into explosive mode. The critical conditions for ignition to occur in a flow can be characterized with the use of the Frank-Kamentnsky

parameter.

$$Fk = Qk(T_{in})R^{2}exp\left(-\frac{E}{R_{g} \hat{T}_{a}}\right) / (\lambda T_{w})$$

A preliminary analysis has yielded the following expression for the critical Frank-Kamentnsky parameter that defines the boundary between the low-temperature and explosive modes.

$$Fk* = \left(\frac{Fk_0^*}{2} - \frac{5}{32}PrEc\right) + \sqrt{\left(\frac{Fk_0^*}{2} - \frac{5}{32}PrEc\right)^2 + \frac{PrEcFk_0^*}{2}}$$

$$Pr = \frac{\mu}{\lambda / (C\rho)}, Ec = \frac{4u_{in}^2}{CT_w}$$
 $Fk_0^* = 3 exp(-1)$

Experiments and numerical calculations confirm that this correlation can be used to predict the conditions that should be realized for a flowing chemically reacting high-viscosity liquid to be ignited.

ON MONOPROPELLANT IGNITION BY ADIABATIC COMPRESSION OF CONTACTED GAS MEDIUM

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The quantitative analysis of monopropellant ignition process at quasiadiabatic compression of contacted gas is conducted within the scope of thermal solid-phase ignition model. On the basis of theoretical research, the influence of external pressure, physical properties of gas medium and thermal-kinetic characteristics of condensed substance on ignition delay are established.

The design of gas generator (with system of start) realizing this effect is considered. The heat-up of air which filled a channel of grain to necessary temperature is produced by fast move of a plunger when certain difference of pressure between environment and closed cavity of grain channel reaches.

The results of preliminary tests of model sample of gas generator verify its workability. The approximate formulae enabling to choose the sizes of channel and sealing plug in accordance with ballistic parameters of monopropellant and operational depth are established.

The absence of cable in this design of gas generator which connect the electric igniter with ground-based power supply, simplifies the thermo-gas-chemical processing of bottom zone of oil-bearing stratum located on large depth with the purpose of increasing its filtration properties.

IGNITION PRESSURE TRANSIENTS IN SOLID ROCKET MOTORS

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The ignition transient is important in many aspects such as guidance and control, structural integrity, reliability and operational repeatability. The ignition transient is studied by approximating the actual configuration to a mathematical model. For ease of analysis, the ignition process is separated into three events namely ignition lag, flame spreading and chamber filling. Each event is studied individually during this work. Flame spreading is studied by thermal analysis of the propellant, the chamber conditions are evaluated by applying equations of mass continuity and energy conservation. Numerical techniques were used for solution of the ordinary and partial differential equations thus obtained along with appropriate stability criteria. Given the pyrogen igniter characteristics and the rocket motor equilibrium operating conditions, it is now possible to predict the ignition behaviour of the rocket motor. The computer program developed was run for different cases, so as to study the effect of different parameters on the ignition transient such as auto-ignition temperature, nozzle blank ejection pressure, internal presurization and use of a oversized igniter. Improvements in the mathematical modelling and analysis of the ignition transient are also discussed.

ANALYSIS OF METALLISED PROPELLANT IGNITION PROCESS UNDER CONDUCTIVE HEATING

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The present work involves theoretical and experimental investigation on the ignition of metallised propellant. Ignition of a composite aluminised propellant (AP-HTPB-Al) in stagnant hot air is analysed theoretically on the basis of gas phase and solid phase theories. By gas phase theory, an exothermic gas phase reaction adjacent to the propellant surface is considered responsible for the ignition. The changes in temperature and concentrations in the gas phase and the temperature profile below the propellant surface during the pre-ignition induction period are considered in the analysis. Equations of energy and concentrations of reactants have been solved to obtain the species concentration and temperature profiles in the gas phase. Ignition, according to solid phase theory, is due to the thermal reaction of the propellant in the solid phase at elevated temperatures. One dimensional transient solid phase energy equation is solved to obtain various ignition parameters. An experimental investigation of the ignition of AP-HTPB-Al propellant is also carried out in a shock tube under end mount conditions. The propellant mounted on the end flange, flush with the inside, is ignited by the stagnant gas behind the reflected shock. The ignition is sensed by a photomultiplier through a quartz window in the shock tube. The time between the arrival of the shock at the end flange and the emission of light due to ignition is taken as the ignition delay. Experiments were conducted in oxygen, nitrogen and air environments. Pressure and temperature ranges covered in the experiments are 6 to 16 bar and 1500 to 3000 K respectively. The comparison of the experimental data with predicted results show that the ignition in an oxidising atmosphere is by gas phase reaction whereas in an inert atmosphere solid phase reaction may be predominant.

IGNITION STUDIES ON ALUMINISED PROPELLANT

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The present work deals with ignition studies on the metallised propellant (AP/HTPB/AI) which is of interest to Indian Space Research Organisation. An experimental investigation has been carried out to determine the minimum ignition energy and corresponding heat flux, threshold heat flux for ignition and minimum ignition temperature. Ignition experiments were conducted using a shock tube (3m/5m) under convective heating conditions similar to those prevailing in a rocket motor. Convective heating of the propellant is achieved in an 8×8 mm square test channel, attached to the shock tube end flange. The other end of the test section is connected to a dump chamber. The high pressure hot gas behind the reflected shock expands through the test section and flows to the dump chamber heating the propellant kept flush with the inside wall. The velocity of flow through the test section is controlled by appropriate orifices fixed at the downstream side of the test section.

Heat flux at propellant location is measured by a thin film heat flux gauge kept in the propellant position. The heat flux gauge is made by applying a thin film of platinum paint of 50–100 ohm resistance over a quartz substrate. The heat flux is measured for different test conditions to calibrate the shock tube. The measured heat flux agrees well with the heat flux computed by the empirical equation for heat transfer to a flat plate. Heat flux is also calculated from a ribbon thermocouple output placed in the propellant position under similar test conditions and the value thus obtained agrees within 15% of the measured one using the thin film gauge.

The arrival of the hot gas at the propellant is detected by a PCB pressure transducer kept near the propellant position and the ignition of the propellant is detected by sensing the light emitted with a photomultiplier tube. The time lag between the two signals was reckoned as the ignition delay. Ignition energy is calculated by multiplying the ignition delay with the corresponding heat flux. For the measurement of ignition temperature, the propellant sample with Chromel-Alumel thermocouple embedded just below the surface is ignited in the test section. The temperature profile of the propellant recorded with the thermocouple forms the basis for deducing the ignition temperature. Deviation to the upward curvature in the temperature profile is taken as the ignition temperature.

The experimental results indicate that the dependence of ignition delay on pressure is almost insignificant. The minimum ignition energy obtained is 1100 J/m^2 corresponding to the heat flux range of $80-120 \text{ W/cm}^2$. The threshold heat flux required to ignite the propellant is 40 W/cm^2 and the threshold ignition temperature of the propellant is $600 \pm 20 \text{ K}$.

COMBUSTION DIAGNOSTICS

STUDY ON THE COMBUSTION AND DECOMPOSITION CHEMISTRY OF HEM BY PROBING MASS SPECTROMETRY

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The main source of our knowledge on combustion chemistry of High Energy Materials (HEM) are the results of flame structure investigations. Recently, great progress in the field of HEM combustion science has been observed. In this paper, the modern state of this problem is considered. The main methods applied to the investigation of chemical structure of HEM flame are probing mass spectrometry and spectroscopic methods. Merits and demerits of both the methods are considered. At present, the most effective and universal experimental technique for studying the HEM flame structure is mass spectrometric probing of HEM flames. It allows the identification of all species present in the flame, including those in the zone adjoining the HEM burning surface and determination of species concentrations as well as their spatial distributions. The data reveal products of condensed phase reactions which are responsible for gas phase heat release as a result of gas phase reactions. The two types of apparatus have been developed for studying the flame structure by microprobe and molecular beam techniques. Time-of-flight and quadrupole mass-spectrometer techniques have been used. Method of probing mass spectrometry is successfully applied for the study of kinetics and mechanism of HEM thermal decomposition using flow reactor. The knowledge of HEM flame structure as well as the kinetics and mechanism of HEM thermal decomposition at high temperature provides a basis for the elaboration of an HEM combustion model. The results of the study of flame structure of RDX, HMX, AP, ADN and AP - double base propellants as well as sandwiches based on HMX and AP at different pressures are presented. The species which are responsible for reactions in flames have been determined. The combustion chemistry of above mentioned HEM is considered. The results of flame structure modelling for RDX, AP sandwiches are in good agreement with the experimental ones. The thermal decomposition studies of several HEM (AP, propellant based on AP, ADN, AN) at high temperature and high rate of heating (i.e at conditions, close to conditions at the HEM burning surface) have been carried out.

INTERFEROMETRIC TECHNIQUE AND OTHER OPTICAL METHODS IN COMBUSTION RESEARCH: NEW APPROACHES AND RESULTS

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Recently, wide potentialities of the interferometry techniques in research to understand the combustion processes in particular propellant burning in terms of process visualization as well as in determining the local and integral burning process characteristics are reported (1–7). The present paper is an attempt to generalize the findings and experimental results of the authors' investigation into the development of new approaches to the interferometric technique in propellant burning research as well as possibilities of adopting other "similar" optical techniques (5). All the techniques and experimental results are discussed in detail in our earlier paper (8).

The new approaches make it possible to assess characteristics of the burning wave which describe the gaseous phase of burning (or burning process as a whole) taken in its entirety and those averaged over the gaseous phase mass (its volume or sections of the gaseous phase flow) so called "integral characteristics". They are evaluated without solving inverse problems of optics, unlike in the case of a number of current methods applied to the quantitative studies of combustion processes. The new approaches rely on the direct employment of the property of integrality of the techniques. For calculation of the "integral characteristics''" the function of the distribution of the quantity is directly measured in the recording plane and the integral derived from this function are used. For example, so far as interferometry is concerned, the following quantities can be determined by measuring the object eikonal (the double integral of the phase difference distribution in the interferogram recording plane) and applying assumptions like limited energy balance equation, pseudo-ID-approximation, small g-phase relaxation time:

- gas mass and enthalpy (isobaric thermal effect) of the gaseous phase of the propellant burning- the "Archimedes lifting force" acting on the heated gas
- non-stationary mass burning rate, heat release power and convective heat flux at the level of the sample surface during ignition of the propellant
- resulting thermal effects of the chemical reactions and the thermal effect of the convective heat loss from the burning sample surface during a propellant ignition process
- conductive heat flux from the g-phase to the burning sample surface
- total work of gas formation and the "force of powder"
- convective heat flux profile, profiles of the average (with respect to the stream section) linear velocity of the gas flow and heat release rate in the stationary reacting gas flow (in the gaseous phase of propellant burning)
- the characteristic time of the individual successive stages of the onset of the ignition process; gasification delay, endothermic and low-exothermic gasification, inflammation of the gasification product
- the response characteristics of the propellant ignition process to the laser radiation interruption (the characteristic times and the thicknesses of the burning-out layers of the individual stages: response of the gaseous phase reaction zone, stage of the delay of the condensed phase response, response of the condensed phase reaction zone, response of the condensed phase heat layer that developed upon exposure to the laser radiation and stage of the establishment of the new level of the burning rate

- the effective absorption index of the condensed phase during a propellant ignition process
- the variation in the mechanical impulse of a non-stationary gas flow and its reactive force (1).

The integral approach based on measuring the integral of the light intensity distribution in the recording plane can be applied to other optical techniques such as emission and absorption spectroscopy, X-ray radiography, light induced fluoroscence technique. Mie scattering technique for following applications (5):

- the total number of the absorbing centres (molecules) in the flame (the methods based on flame absorption measurement)
- the total number of chemical unit acts occurring in unit time and involving emission of a quantum with known energy (emission measurement of the chemiluminescence)
- the average particles diameter in a dispersed flow (Mie scattering technique).

The paper also deals with new approaches to the traditional problem of the quantitative interferometry i.e. to the definition of flame temperature fields [in this approach any change in the flame gas mixture composition is taken into consideration for a variety of gaseous and condensed systems based on general principles (7)] and qualitative interferometry [the holographic interferometric cine-films visualizing the ignition process of transparent (glassy) propellant models both in the condensed and the gaseous phases which has enabled the sequence of practically all the process stages to be traced more closely (6)]. The present paper generalizes all experimental data obtained.

Undeniable advantages of interferometry for diagnostics of combustion are non-intrusiveness, fast response, and obviousness. But in our opinion its most fundamental advantages are a wide spatial and temporal range of measurements (determinability of both local and integral characteristics) and possibility to determine a wide variety of characteristics.

The authors hope that the joint efforts of the authors and of those workers who will take interest in the practical implementation of interferometry potentialities will permit the solution of number of problems of the combustion research. The authors would like to invite experts in the fields of combustion research to participate in the interferometry-related projects framework.

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STUDIES ON FLAME SPREAD WITH SUDDEN EXPANSIONS OF PORTS UNDER ELEVATED PRESSURE

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The flame spreading process is known to significantly influence the initial part of the thrust or pressure transient. The mechanism of flame spread, apart from being dependent on the thermal characteristics of the propellant, is influenced by the heat transfer processes which in turn depend on the flow, ambient conditions and propellant geometry. Normally, flame spread mechanism is assumed to be smooth or continuous. But this is not true in a many practical rocket motors such as Dual Thrust Motor and PSLV third stage motor where flow separation, recirculation and reattachment exist. This will alter the convective heat transfer and hence the flame spread mechanism. The process of flame spread through such a port which is an input to any model, remains an unknown factor. In the present experimental work, the sudden expansion region is modelled/simulated as a backward-facing step.

A laboratory size solid propellant window motor was designed to withstand an elevated pressure of 500 N/cm². Freshly prepared rectangular cross-sectional HTPB propellant was used for this study. The controlling factors for the flame spread in the present experimental programme are the step height, step location, port height and chamber pressure. Data generation, both qualitative and quantitative, is through frame - by - frame analysis of the cine photographic records obtained at a speed of 64 PPS. Location of the main flame front at different instants of time constitute the raw data from which the rate of flame spread, occurrence of secondary ignition and other information are deduced.

Some results at ambient atmospheric conditions have been reported earlier. In the present paper, additional results at high ambient pressures are discussed. Compared to the tests conducted at atmospheric pressures, the relatively shorter time scale and higher velocity levels are evident at elevated pressure tests.

It has been shown conclusively that under certain conditions of step location and port height which govern the velocity of gases at the step by the partially ignited propellant surface, secondary ignition may occur far downstream of the step. This is very likely to be a region of reattachment of flow. The secondary ignition gives rise to two additional flame fronts one of which spreads backward at a relatively lower velocity presumably due to the low reverse velocities present around the separation zone. This phenomenon is likely to play an important role in the ignition transient of solid propellant rockets with non-uniform ports.

The effect of secondary ignition will be accentuated in the case of star grain downstream of sudden expansion where the star points generate multiple flame fronts. The effective time required for the complete burning surface area to be ignited will be altered drastically giving rise to an altered pressurization rate (dp/dt) in the second phase of ignition transient.

A detailed numerical simulation of the flame spread has also been carried out with the help of P(t, x) model. The results corresponding to the above experimental configuration and propellant properties reproduce many qualitative features such as secondary ignition and backward flame spread. Further work is needed to study the influence of this flame spread behaviour on the overall ignition transient.

It may be inferred from this experience that the phenomenon of flow separation and reattachment could also modify the nature of erosive combustion which also adds to the complexity of the ignition transient.

APPLICATION OF ULTRASONIC TECHNIQUE FOR MEASUREMENT OF INSTANTANEOUS BURN RATE OF SOLID PROPELLANTS

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In the conventional methods of burn rate measurement of solid propellants (like the strand burner and ballistic evaluation motor) the burn rate is determined by monitoring the time taken for burning of an initially-known thickness of propellant. These methods give the average burn rate of the propellant specimen or grain, but do not give the local burn rates inside the propellant. Hence, any abnormalities in burn rate within the grain are not brought out quantitatively by these methods. Further, since each test gives only one value of burn rate at the test average pressure, determination of burn rate index (in the power law for burn rate versus pressure) necessitates conduct of several tests, each of them at a different pressure. These drawbacks of the conventional methods can be overcome if a measurement technique is used wherein the instantaneous burn rate is determined as the propellant web burns. The ultrasonic pulse-echo technique is one such technique. This has been recently used by us for burn rate measurement in aluminized composite propellants. This paper presents the principle of the technique, its application by us to solid propellant burn rate measurement, the data processing and results.

The ultrasonic technique is based on the property of ultrasound that the acoustic wave reflects (partly) at any interface encountered, where local acoustic impedence changes. Using this property, the ultrasonic technique is employed to determine instantaneous thickness of propellant web during burning by means of 'pulse-echo technique' in which same probe (transducer) acts alternatively as an emitter of pulse and a receiver of echo pulse. It involves transmitting of ultrasonic signals through the web of propellant grain which are reflected back at the burning surface. The elapsed time for the ultrasonic signal to return through the web gives the instantaneous thickness of propellant web and thereby the burn rate, if sound velocity in the propellant is known.

The Pulse-echo Interface Measurement (PIM) system employed by us uses an ultrasonic transducer operating at 2.25 MHz. The ultrasonic pulses are emitted and received through the transducer at the maximum rate of 5 kHz. For the linear operation down to zero propellant thickness and to isolate the transducer from severe pressure and temperature conditions of the motor, an intermediary coupling element is introduced between the propellant and the ultrasonic transducer. A proper selection of transducer, coupling material and proper bonding of coupling element to the propellant were important factors for the successful application of the technique. Also, an accurate determination of sound velocity in propellant/coupling material and the effect of temperature and pressure on sound velocity in the material also had to be determined.

In this phase of the study, tests on end burning propellant specimens were carried out. Instantaneous burn rates of HTPB based aluminized (18% Al) composite propellant specimen (end burning) of 30 mm thickness were measured at nearly constant pressure in a laboratory set-up using ultrasonic technique. The measured burning rate was also compared with the burn rate obtained from ballistic evaluation motor (using web thickness and motor burn time) cast with propellant of same batch mix. An accuracy of burn rate measurements of \pm 1% was achieved and excellent reproducibility of results was established.

METHOD TO DERIVE SOLID PROPELLANT EROSIVE BURNING RATE USING REACTIVE MOTOR PRESSURE DIAGRAM

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An experimental - calculating method is proposed to derive the local erosive burning rate and other characteristics of solid propellant combustion using correlation between the combustion rate and the pressure diagram of semi-closed chamber. Such correlation is established employing the physico-mathematical model of the interior ballistic process in rocket motor taking into account dependence of the unsteady combustion rate on local values of pressure and gas flow velocity as well as on ignition conditions. The possibility of obtaining new data on the combustion and ignition process and also of correcting the data taken from experiments on combustion in constant volume bombs is demonstrated for selected double base propellant charges with the tubular elements.

COMBUSTION MODELLING

IGNITION AND COMBUSTION OF THE DISPERSE SYSTEMS

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The combustion problems of the disperse heterogeneous systems (DHS) are the focus of attention of researchers for the past thirty years. The reason of such interest is that these combustible systems are used widely in energetized technological processes, propellants, pyrotechnic compositions and so on. Accordingly, the fundamental research in the area of ignition, combustion and extinction of the DHS has gained importance. The aims of the investigations are to find the conditions of the crisis phenomena origin, determination of the typical time process, efficiency and combustion temperature regimes. In this review, present status of application of combustion physics (theory and experiment) in the field of DHS and perspectives of its further development are analysed.

In the first part, typical DHS features are shown which ascertain the specificity of their ignition and combustion, developed reactive surface, oxidic films, fuel and oxidizer phase transformation, possibilities of particle reacting in different regimes and at varied temperatures.

Second section deals with the conditions of DHS ignition with different fuel oxidation laws. The criteria binding environment and fuel parameters in critical conditions are given. It is shown that the fuel activity (A = $1/\gamma_0$, where $\gamma_0 = C_p T^2/qE$ is the parameter of Frank-Kamenetskii) for disperse systems essentially depends on the ratio of reactive

surfaces and heat exchange surfaces : $A^* = \frac{1}{\gamma_0} S_r / S_H$. In this approach, part of the parallel heterogeneous reactions

in DHS ignition is considered. The influence of the evaporation on the ignition nature is shown taking the example of boron DHS ignition.

In the third section, the possible particle combustion regimes (heterogeneous, vapor-phase, gas-phase) are analysed and the peculiarities of the dust clouds combustion (competition between the oxidizer depletion and self-heating of system and its part in dynamics of the dust clouds combustion) are discussed.

In the last section, the extinction conditions for single particles and dust clouds is considered taking into account parallel heterogeneous reactions. Adequate criteria and computer results are quoted. The influence of media parameters on extinction conditions of particles has also been analysed.

In conclusion, the attempt to formulate the further steps in studies of DHS combustion is discussed.

COMBUSTION SIMULATION FOR MELTING ENERGETIC MATERIALS

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One-dimensional transient model of combustion of melted energetic materials (EM) has been developed. The model describes heat propagation in both condensed and gas phases with chemical reactions of the first order proceeding in the condensed phase and of the first and second order proceeding in the gas phase. The condition of equilibrium evaporation in the form of Clausius-Clapeyron equation is assumed as matching at the interface between condensed and gas phases.

The analysis of steady-state combustion regimes revealed an intrinsic combustion instability for energetic materials with relatively weak heat feedback from gas phase that leads to the appearance of temperature maximum in the bulk of condensed phase. This conclusion was made on the basis of the analytical study by small perturbation and matched asymptotic expansion methods and was confirmed by numerical calculations.

Numerical calculations of EM combustion with thermal and kinetic parameters imitating the RDX properties have shown that the radiation-driven ignition occurs in two different modes depending on the intensity of irradiation. At low radiant fluxes the ignition follows classical pattern with successful transition to self-sustaining combustion after removal of external energy source. At high radiant fluxes, the regime of relatively slow condensed phase pyrolysis-evaporation is established with heat feedback from gas phase being negligibly small. Sharp cutting off of the radiant flux leads to extinction. However, transition to self-sustaining combustion can be achieved under gradual decrease in time of the irradiation intensity.

Increase in the EM transparency (decrease in the extinction coefficient) leads to formation of temperature profile with maxima in the bulk of material and to explosion type decomposition of subsurface layer at the first stage of ignition followed by unstable combustion even under constant irradiation. Enhancement of thermal conductivity in melt layer results in translucent EM in normal ignition transient behavior with two stage transition to self-sustaining combustion.

Comparison between experimental data on stationary and transient combustion of pressed RDX samples and results of calculations within the framework of the developed model showed good agreement.

PARTIAL BURN LAWS IN PROPELLANT EROSIVE BURNING

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A set of experimental and computer methods was developed in previous works of the authors for investigations of combustion phenomena in propellants which burn in a stream of hot gas flowing along the burn surface of different propellants. The experimental investigations performed mainly by micro thermocouple technique allowed determination of different dependencies for erosive burning to be obtained. Computer solving of heat conductivity equation within the framework of Zeldovich-Nivoshilov's theory showed a very good coincidence with experimental results. The suggested variant of the theory takes into consideration the change of heat release in solid, the real burn surface roughness, nonisothermality of the boundary layer and the effect of gas mass flow from the propellant burn surface into the gas stream. This theory was used for studying burn laws in a wide range of pressures (from 30 up to 2000 atm) and gas stream velocities (up to that of sound) for double base propellants with different caloric powers. It was found that gas stream leads to the splitting of burn laws: in the formula m = bp^v, pressure power v in this case depends on gas stream velocity w, diameter of propellant tube channel d (on granular diameter d - for granulated propellants) and on gas stream temperature Ta. Due to this, these burn laws were named partial burn laws. They have the form $m_p = bp^w$ at constant w, d and T_a . The dependencies $\omega = f(w,d,T_a)$ were obtained in this work under the conditions mentioned above. It was found that values of ω mainly decrease when pressure increases beginning from 200-300 atm and they can decrease up to $\omega = 0.2 - 0.3$. Similar values of ω can be obtained for composite propellants. Such values of ω are of great industrial importance.

AN APPROACH TO COMBUSTION MODELLING OF ENERGETIC BINDERS IN SOLID ROCKET PROPELLANTS

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A composite solid propellant is a mixture of crystalline oxidiser (generally AP/nitramine), polymeric fuel cum binder (polybutadiene, azido polymer, NC/NG matrix), metal powder (generally Al), burning rate modifiers, processing aids and curatives. The combustion of such a heterogeneous mixture is a highly complex phenomenon involving many subprocesses. The key processes which control the burning are heating of the condensed phase, degradation of the oxidiser and fuel, possible melting, vaporisation, mixing in the vapor phase and gas phase combustion. A composite propellant can be looked at in two ways. One way is considering an oxidiser surrounded by the rubbery continuous matrix and analysing the evolution of vapor from such a "two-source" system. As per the other consideration, the evolution of vapors is largely dominated by the AP. Relatively small proportion of the binder has been known to profoundly influence the combustion process. Hence, it is intended to study the effect of different binders namely, hydroxy terminated polybutadiene(HTPB), epoxy resin and GAP. Beckstead-Derr-Price (BDP) model for the combustion of composite propellants has been the basis for most propellant modelling studies for the past several years. It was originally developed for monomodal AP composite propellant, but has been adopted by various workers to multimodal oxidisers, HMX propellants and a variety of other modifications. A basic assumption of the original model is that the surface temperature of the propellant is averaged over both oxidiser and binder. This assumption implies the subordinate role of the binder in BDP approach. In the present attempt, an independent surface temperature for the binder is considered. The surface temperature of the binder is given by

$$\xi_{pF}^* = \frac{C_p \cdot m_T \left(\overline{x}_{pD}^* + x_{pF}^*\right)}{\lambda}$$

$$\xi_{Ap} = \frac{C_p \cdot m_{ox} \cdot x_{Ap}^*}{\lambda}$$

The flame stand off distances are calculated as per BDP model

$$T_{SF} = T_0 - \frac{F_{rb}Q_{Fuel}}{C_p} + \sum_{i,j} (1 + \beta_{pi,j})F_{rb}P_{Fi,j} + (1 + \phi_{SF})\frac{Q_{pFi}}{C_p} \cdot e^{-\xi_{pF}^*} + \beta_{DB} \cdot \frac{Q_{DB}}{C_p} e^{-\xi_{DB}^*}$$

The fraction of the oxidiser reacting in the primary flame is also calculated as in the BDP model. In the present study the monomodal AP of 4 microns and 10 microns particle sizes along with HTPB, epoxy resin and GAP have been considered. The theoretical results arrived at are found comparable with the practical results obtained by using acoustic burner technique.

This study also establishes the validity of the basic assumptions and understanding of combustion process in AP-CMDB propellants.

REGIMES OF COMBUSTION OF SOLID POROUS ENERGETIC MATERIALS

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Two basic regimes of exothermic transformation of solid energetic materials are usually distinguished: deflagration (or slow combustion) and detonation. The rate of combustion of solid propellants is usually rather low and thermal conductivity is the main factor governing flame propagation processes. The rate of detonation of solid energetic materials is usually very high, ignition of the successive layers of material takes place due to their compression in a shock wave sustained by chemical energy release. Thus, the shock wave propagation in solid energetic materials is the main governing factor that drives reaction zone during detonation. Theoretical and experimental investigations of macrokinetics of chemical transformations in high energy materials reveal that depending on the structure of material there exist several intermediate regimes that differ greatly from deflagration and detonation in velocities and mechanisms of flame propagation. The present paper is devoted to multiplicity of scenario of flame propagation in solid high energy materials.

The existing porosity of high energy materials can cause acceleration of flame propagation, rapid increase of pressure and combustion rate. Heated reaction products penetrate the pores igniting the surface. The increase of the burning surface causes increase of pressure in the pores that promotes further convective flow of reaction products deeper inside the pores. Thus, mechanism of flame propagation changes from a conductive one to a convective one when flame propagation velocity is determined by a convective flow of heated reaction products inside the pore.

High pressures arising in pores cause compression waves in gas and solid. When the intensity of compression waves in gas phase is high, the ignition of energetic material can take place on the surface of the pore due to its heating by a shock wave compressed gas. Convective regime of flame propagation evolves into a new regime governed by compression wave propagation in gas phase inside the pore. This self-sustaining regime is characterized by flame velocity that is supersonic as compared to sound velocity in gas phase but subsonic as compared to velocities of weak disturbances in solid material.

If the intensity of shock waves in solid materials is high enough to cause plastic deformations and the sensitivity of energetic material is also rather high, the dissipative heating can cause ignition of energetic material in so-called "hot spots" that lead to formation of the regime of low-velocity detonation.

The further increase of pressure in the leading shock wave can bring about normal detonation in energetic material. The presence of rather wide pores of channels in sensitive energetic materials leads to an effect where expansion of reaction products forms gas cumulative jets inside the pores that overtake the detonation wave. Those jets sustain shock waves initiating detonation on the surface of channels. The so called "channel effect" occurs when velocity of detonation wave in energetic material surpasses the equilibrium velocity of Chapman-Jouget detonation for this material.

To investigate the variety of regimes of combustion in solid porous energetic materials, a mathematical model of wave dynamics for two-phase porous medium is worked out taking into account the deformation tensor for solid phase, mass momentum and heat exchange on phase interfaces and dynamics of energy release.

MATHEMATICAL MODELLING OF IN-CHAMBER PROCESSES IN HYDROCOMBINED SOLID ROCKET MOTORS

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The engineers of the National Rocket Center "The Makejev Design Office" and the scientists of the Tomsk State University are working on designing commercial rockets launched from a water surface. The special conditions of employment of such rockets, when the environment is sea water open up new possibilities of improving motor performance. The most interesting method suggests supplying water into the running motor. This paper reports the calculations and experiments carried out with solid propellant model set-ups.

The results prove the validity of the proposed method and allow the refinement of calculation techniques for the prediction of SRM performance characteristics. The serviceability of the solid propellant charges working in combination with water is demonstrated. A mathematical model is proposed for the operation of a hydrocombined propellant motor with water and powdered additives applied to the combustion chamber.

NUMERICAL SIMULATION OF INFLUENCE OF SOLID ROCKET PROPELLANT COMBUSTION PRODUCTS ON THE UPPER ATMOSPHERE

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It is known that on launching of a rocket, considerable amounts of gaseous and condensed combustion products are emitted that exert a harmful effect on the environment. The most ecologically dangerous components of the solid-propellant combustion products are nitrogen oxides and chlorine produced in large amounts. It is also known, that the high-temperature exhaust gas stream conditions and the physico-chemical processes in the nearest trail of combustion products largely determine the degree of the effect on the ozone balance in the upper atmosphere.

To model the relevant chemical processes, advection and diffusion, we must write three-dimensional timedependent equations for diffusion of constituents, taking into account the chemical reactions that proceed in the middle atmosphere:

$$\frac{\partial \rho C_i}{\partial t} + u \frac{\partial C_i}{\partial x} = \frac{\partial}{\partial x} \left[D_x \frac{\partial C_i}{\partial y} \right] + \frac{\partial}{\partial y} \left[D_y \frac{\partial C_i}{\partial y} \right] + \frac{\partial}{\partial z} \left[D_z \frac{\partial C_i}{\partial z} \right] + \phi_i$$

where C_i is the concentration of i th component: O_3 , C_1 , C_1 O, C_2 , C_3 O, C_4 O, C_5 O, C_6 O, C_7 O, C_8

Thermodynamic analysis of combustion products was carried out for three compositions of solid rocket propellant of all components of gaseous combustion products generated on the height of 25 - 35 km, where ozone concentration is the highest and only atomic chlorine takes part in the destruction of ozone. Nitrogen oxides present in small amounts have small influence on the state of the ozone layer. Therefore, at z > 25 km the major mechanism of ozone depletion is associated with chlorine cycle. However, in the tropopause and lower stratosphere the role of nitrogen oxides found in exhaust products is fairly significant in this regard and neglect of nitrogen contribution to ozone depletion may introduce large errors.

Our investigation offers an opportunity to analyse the influence of solid rocket motors combustion products on the state of the ozone layer and provides an estimate of ecological danger of rocket and space vehicles launching.

MATHEMATICAL MODELLING OF THE NONSTATIONARY PHYSICO-CHEMICAL PROCESSES ACCOMPANYING THE COMBUSTION ABNORMAL MODE IN THE LARGE- SIZED SPRM PYROTECHNICAL IGNITION SYSTEM

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The intraballistic parameters in the initial stage of operation of the large-sized solid propellant rocket motor (SPRM) in many respects are determined by the physico-chemical processes proceeding in the ignition system (IS) and subsequent heat effect of the IS charge combustion products (CP) on the motor main charge. That is why, it is important to know how to calculate accurately parameters in the IS and especially, taking into account the possibilities of appearance of the combustion abnormal modes.

In the present paper, the laws of the unstable wave processes accompanying the combustion abnormal mode in the large-size SPRM pyrotechnical IS is investigated numerically. The IS contains the main cylindrical channel (MC) having uniform perforation over the lateral surface. The left MC boundary is deaf and in the right boundary there is uniform perforation. The whole perforation is hermetically sealed outside. The additional cylindrical channel (AC) (an initial impulse amplifier) with uniform perforation over the lateral surface is installed into the MC cavity, coaxially to MC. Granulated elements having the spherical form and pressed from the pyrotechnic mixture are placed with the bulk density in the cavities of the channels (AC and MC). The right AC boundary is deaf and the time-varying high-temperature gas flow, containing incandescent particles is supplied from initiator, equipped with a fast burning compound, through AC left perforated boundary. Ratios of channels' length to their diameters are more than one and preset to be equal to 1.2 - for MC and 10 - for AC. To imitate the exploitation conditions the IS is placed in a cylindrical imitation chamber. The process in the IS and then in the imitation chamber is developed in the following way.

From the initiator, CP arrive at AC, where they heat-up and ignite the pelletized propellant. From the AC, the CP arrive in the MC, where they heat-up and ignite the pelletized propellant. When the pressure in the MC achieves the level, exceeding the destruction pressure of the hermetic sealing, destruction of the hermetic sealing occurs and the CP begin to arrive in the imitation chamber.

In a number of cases, before the beginning of the IS operation, a situation can be realized when the granulated propellant (GP) mass is non-uniformly distributed along the IS AC length, and the greater part of the AC lateral perforation is blocked by the GP inserted in the IS MC. These conditions may lead to the pressure waves of abnormal strengthening at the AC boundaries.

When constructing the mathematical model of gas dynamics processes proceeding in the AC IS the assumptions system accepted in our earlier work (1) is used. The physico-chemical processes proceeding in the initiator, IS MC and in the imitation chamber are simulated in the thermodynamic statement (2). One-dimensional gas-dynamic equations of motion of the CP mixture between the granulated elements, are written for the multicomponents biphase mixture of the ideal gases. A peculiarity of the model is that the physical processes accompanying the CP filtration through granular propellant are taken into account. The boundary conditions are realized in the gas-dynamic problem in accordance with earlier published findings (2). For the description of the hydrodynamic processes and heat exchange processes in the porous medium, the procedure adopted during this work is based on the model of the integral characteristics of systems (1). Calculation of the temperature state of the solid phase and its non-stationary burning-out is carried out in accordance with the model of the Russian scientist R.Ye Sorkin (3). The heat problem written down in the one-dimensional form, is solved in each of gas-dynamics knots for a separately taken propellant

pellet. Integral dependences suggested by the Russian scientist V.P.Bobryshev (2) are used to account for the possible erosive effect in GP burning. The equations, describing the gas-dynamic processes, are solved numerically by the Large Particles Method, developed by the Russian scientist Davydov (4) after a number of modifications (2). To increase the stability and precision of the numerical calculations, the Euler stage of the method is modified in the regions of the low velocities of the filtrating CP.

For the complex check-up of the developed mathematical model of physico-chemical processes, the numerical calculation results have been compared with the fire stand tests.

The analysis of results of numerical investigations of laws of the physico-chemical processes evolution in the pyrotechnic IS AC reveals that the pelletized propellant inflammation occurs under substantially nonstationary conditions. Processes of flame front propagation over the GP surface and their following joint nonstationary and erosive combustion have pronounced temperature sensitivity. The numerical analysis of the unstable wave development in the AC has shown that the rise of the pressure with an ever increasing amplitude are realized at the moments, when a shock wave reflects alternately on the left and on the right AC boundaries. The amplitude of the serial pressure that rises at the AC boundaries can exceed the average pressure level 3-6 times. The effect of the pressure waves' abnormal strengthening can result in the destruction of the AC and other elements of the IS structure and exert unfavourable influence on the development of the ignition process of the SPRM charge. In particular, the SPRM propellant charge may not ignite at all. Moreover, the appearance of the intermittent burning ("chuffing") mode is possible. The "chuffing" is most probable in the small sized SPRM as well as in the large-sized SPRM with a high intrachamber loading coefficient.

The influence of the initial non-uniform distribution of a granulated charge was for the first time investigated in the ordnance science, even in the last century. These investigations were executed by Major-General of the Russian Army Nickolay V.Kalakoutsky. The program of his investigations included several thousands of experiments (1876-1878), directed on the search of the most rational method of realization of the powder tests of the steel gun barrels. On the basis of the numerical analysis results, the pyrotechnic IS construction scheme is elaborated during this work. This IS scheme has an increased operation reliability. The reliability is enhanced by means of the suppression of the described abnormal effect. To provide this, the IS AC (the central perforated tube) is executed multisectionally and each of the sections is supplied with granulated solid propellant. Prior to the beginning and during the GP ignition period all mentioned sections are inter-connected gas-dynamically. After GP ignition in each of the sections, the cavities of these sections are automatically isolated one from another and the GP burning lasts in each of the isolated sections. Thus, the possibility of the shock waves propagation along the IS AC cavity and accordingly, the occurrence in the IS AC cavity of the effect of the pressure wave self-strengthening up to the values, considerably exceeding normal level, is excluded.

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PYROLYSIS-CAUSED TAIL OFF THRUST IN A SOLID ROCKET MOTOR: AN EMPIRICAL MODEL AND ITS APPLICATION TO FLIGHT SEQUENCING

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Separation of a spent stage is an important event in the flight sequence of a satellite launch vehicle. It is a critical event when the spent stage is a motor which makes use of solid propellant. This is mainly because of the presence of the 'tail-off thrust'. The impact of tail-off thrust is all the more significant when the motor is used for an upper stage as in the case of the stage 3 motor of the Polar Satellite Launch Vehicle (PSLV). This is because the tail off thrust, though small, can accelerate the spent stage to a greater extent in the case of an upper stage, where its mass is considerably less compared to that of a booster stage. If the flight sequence is not properly designed, there is a chance of the tail off thrust causing the spent stage to speed up and recontact with the ongoing part. For a proper design of the flight sequence, it is very essential to have a prior knowledge of the tail off thrust. Unfortunately, no accurate theoretical or empirical model is available for the tail off thrust. Based on the vehicle acceleration data, obtained over a short duration in the second developmental flight of PSLV, the authors could develop an empirical model for the tail off thrust. This was applied for flight sequencing of the third developmental flight, namely PSLV D3, and was validated using the data from this flight.

The tail off thrust has two major characteristic regions, one corresponding to the burning of the left out propellant and the second corresponding to the pyrolysis of the motor lining material. A major break-through was achieved by the authors by evolving a method for identifying the start of prominence of pyrolysis effect and then for modelling the tail off thrust.

The paper presents briefly the method of establishing the region of prominence of pyrolysis, the tail off thrust model and its validation.

COMBUSTION OF METALLIZED HEM

EXPERIMENTAL INVESTIGATION OF BORON AND BORON OXIDE EMISSIVITY

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The paper presents the results of experimental determination of boron and boron oxide (B_2O_3) over the surface temperature (T_S) range of 1400 - 2000 K. The measurements were made with a joule-heated boron filament $(d=100-300~\mu m)$ coated with the boron oxide layer of the thickness of h < 100 μ m in the helium gas background at two pressures, P=10Pa and $P=1.05\times 10^5~Pa$. The surface temperatures were determined using bichromatic and precision brightness pyrometers.

As direct measurements of the transparent boron oxide layer emissivity, $\varepsilon_{B_2O_3}$ were difficult, the value was checked using the experimental value of boron oxide absorptivity, $k_{B_2O_3}$. The boron oxide emissivity as a function of $k_{B_2O_3}$ was given by the solution of the radiative transport equation for a uniform layer. Scattering of radiation was ignored. The influence of underlayer material on the values $k_{B_2O_3}$, was examined in the experiments with wolframium and alumel filaments of same diameters. The boron oxide absorptivity value is found to be $k_{B_2O_3} = 2.5 \pm 0.3 \times 10^2 \text{m}^{-1}$ and is dependent on the surface temperature over the measured temperature range. For the B_2O_3 film thicknesses which forms under boron ignition (h = 0.1–1.0 µm), this value of the B_2O_3 absorptivity corresponds to emissivity values $\varepsilon_{B_2O_3}$ of 2.5×10^{-5} to 2.5×10^{-4} .

The emissivity of a clean boron surface was determined while heating the boron filaments placed between the turns (D = 2 mm) of wolframium coil. The cleaning of boron surface was achieved by its preliminary heating up to T_s = 2200K in helium medium at the gas pressure of P = 10 Pa. The measured brightness temperature of wolframium coil and boron filament made it possible to determine the clean boron surface emissivity, ε_B = (0.25 ± 0.05). Therefore, in numerical calculations of the boron particle radiation during its ignition, the boron oxide radiation can be ignored.

THE EXPERIMENTAL STUDY OF ZIRCONIUM DUST COMBUSTION IN A FLOW

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The combustion of zirconium dust in a laminar flame is experimentally investigated in this work. The main experimental methods of investigation and analysis were optical spectroscopy, electrical logging, photography, X-ray analysis, particle size and chemical analysis. Two essentially different stable combustion regimes have been observed depending on flame type nonpremixed or premixed. In the first case, the end combustion products are monolith spherical oxide particles with a size which is close to initial metal particles size and in the second case products are nanodispersed powder (zirconium oxide particles size is $0.03~\mu$) in addition to hollow ZrO_2 spheres.

The information on the time of Zr particles combustion in flame, and the temperature of metal particles, condensed oxides, gas phase products as well as the electrical conductivity of combustion zone was obtained.

It is shown for both types of flames that zirconium particles burn individually in a flame. The analysis of experimental data shows that in diffusion dust flame heterogeneous combustion of Zr particles takes place. Moreover, there is gas-phase combustion which is analogous to the combustion of carbon and boron at high temperatures in premixed flame. This difference causes the peculiarity of the second flame regime which consists of the condensation zones localized around each of the metal particles.

The oscillations of luminosity and combustion zone electrical conductivity have been observed in the flame when fuel was premixed with oxidizer. The modulation depth of luminosity oscillations is about 50% and of conductivity oscillations ~ 100%. The frequencies of luminosity and conductivity oscillations are the same.

MAGNESIUM AND BORON COMBUSTION IN A HOT STEAM ATMOSPHERE

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In future, fossil fuels will be in short supply and the world must turn to other basic energy sources. Hydrogen is the obvious technological choice. In this study, we investigate the hydrogen production during direct magnesium and boron combustion in a hot steam atmosphere.

Analysis showed that from the point of view of the hydrogen and the reaction heat evolved during metal combustion, magnesium and especially boron are the main metals of interest. The intensive oxidation reaction of steam with magnesium and the ignition of Mg in H₂O are well known; on the other hand, the high-temperature reaction of boron with water has not been studied in detail. A special facility for the realization of the combustion of Mg and B powders in H₂O and determining the amount of hydrogen evolved in the process was developed.

It was determined that reaction temperatures of Mg and B with steam are about 1350 and 1100 K respectively. The time dependence of gas evolution during the reaction process is obtained. The composition of the gases evolved was determined by a gas chromatograph equipped with a thermal conductivity detector. The relation of areas of the appropriate hydrogen peaks for standard specimens and for check sample points to very high hydrogen content in the gases evolved after metal combustion (about 100%). The hydrogen yield obtained in these experiments accounts for no more than 60% of the theoretically possible one. Additional research is required for increasing the hydrogen yield. The temperature of metal and steam, the size and form of the oxidizable samples, the method of their supply to the burning chamber, as well as the relation between mass flows of metal and steam can be varied to provide a complete and stable yield of hydrogen.

EXPERIMENTAL STUDY OF A METAL LAMINAR DIFFUSION DUST FLAME

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Experimental studies of the combustion of high-energy metal dust (Al, Zr, Ti) in a laminar flow nonpremixed with oxidizer, i.e. in a laminar diffusion dust flame (LDDF) conducted at Institute of Combustion in recent years are generalized. The steady-state LDDF is not only a simplified model of the turbulent flames which are realized in energetic systems and high-temperature two-phase reactors, but also is a very convenient object for investigation of the mechanisms of processes which occur in metal dust combustion. For these reasons, the characteristics of a metal LDDF were investigated using flow reactor technique based on the dust burner, photography, high-speed filming, direct flame sondage, gas analysis, holographic interferometry and optical spectroscopy. The tests were carried out at atmospheric pressure and covered the oxygen volume fraction in oxidizing gas flow interval $m_{ox} = 0.2 - 1.0$, the particle size interval $d_p = 2.7 - 15.0 \mu m$ and the metal dust mass concentration interval $C_M = (0.15 - 0.65) \cdot 10^{-3} \text{ g/cm}^3$.

The experiment confirmed our supposition, which has been reported earlier, that the main distinctions between the LDDF and diffusion gas flame are no counter-diffusion of disperse fuel to gaseous oxidizer, and discrete LDDF burning zone i.e. combustion of metal dust takes place on/near the surface of individual metal particles. The measured width of burning zone is greater than those of a gas diffusion flame. The dust flame length versus parameters of dispersed fuel and gaseous oxidizer have been investigated and it was shown that in a wide range of these parameters the rate of dust burnout in LDDF is controlled by external diffusion of gaseous oxidizer to the burning zone. Connection between the metal particle burning regime and condensed burning products has been found out and identified experimentally. In conditions where heterogeneous combustion takes place, mean size of oxide particles is near initial metal particle size. If vapor-phase or gas-phase combustion is realized, predominant fraction of condensed products is ultradisperse powder ($d_{ox} < 0.1 \mu m$). The hypothesis and mathematical models of LDDF and oxide condensation processes have been formulated on the basis of experimental data.

THE THEORETICAL MODEL OF A ZIRCONIUM PARTICLE COMBUSTION

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The theoretical model of the zirconium particles gas-phase combustion has been deveoloped during this work. The model takes into account the essential peculiarity of the condensation process of intermediate gaseous zirconium oxides.

On the basis of analysis of the condensation zone stability, the conditions of a gas-phase zirconium combustion existence and the probable size of the oxide powder particles are determined. It is shown that size is less sensitive to external conditions and dependent on initial metal particle size. It has also been shown that the presence of condensation zone around a metal particle leads to reduction of gas diffusivity ($D_{eff} \sim D_0/10$, D_0 - diffusivity without condensation zone) that essentially influences the calculated values of zirconium particle burning time.

It follows from the model that heat fluxes balance at zirconium particle surface results in the surface temperature corresponding to phase equilibrium of Zr–ZrO₂ system. The calculated zirconium particle burning time and temperature of condensed combustion products are in satisfactory agreement with the experimental data. The presence of hollow spheres in the products of dispersed zirconium combustion has been explained in this paper.

SYNTHESIS AND CHARACTERIZATION OF ENERGETIC MATERIALS

EFFECT OF TAMMANN TEMPERATURE AND RELATIVE HUMIDITY ON SAFETY AND COMBUSTION OF SMOKE AND FLASH COMPOSITION BASED ON LEAD CHROMATE AND MAGNESIUM POWDER

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One of the primary concerns in the handling of pyrotechnic mixes is the accidental ignition. Ignition of high energy mixtures occurs when the reactants acquire activation energy to be in a reactive state. An ignition stimulus starts a sequence of preignition reactions involving crystalline transitions, phase changes or thermal decomposition of one or more of the ingredients. In many pyrotechnic mixtures, a gaseous phase is formed and combustion starts in gaseous phase. The rate at which a reaction proceeds is determined by the energy barrier that must be crossed ie. the activation energy. Rate is a temperature dependent phenomenon. As the temperature of the system is raised exponentially greater number of molecules will possess the necessary energy of activation. The reaction rate will, therefore, increase accordingly in an exponential fashion as the temperature rises.

Whether a reaction is spontaneous or will actually occur, when the fuel and the oxidants are mixed together is determined by a quantity known as free energy change ΔG . The criterion of spontaneity is:-

$$\Delta G_{T, P} < 0$$

At ordinary temperatures, entropy effects are small so they have little effect on the direction of a chemical reaction unless the difference in ΔG between reactants and products is relatively small. However, in a pyrotechnic combustion reaction at higher temperatures there is significant difference in the free energy change of reactants and the products. Hence, all chemical reactions which involve an increase in entropy will occur spontaneously if the temperature is high enough. Pyrotechnic reactions often involve the oxidation of a metal to form a refractory oxide. The reaction is reversible and the degree of decomposition will depend on the oxygen partial pressure as well as the temperature. According to Le Chatlier's Principle, in this type of decomposition in a confined system, the partial pressure will increase and the reaction will shift to the left. A high temperature is therefore required to decompose the oxide. To set off a pyrotechnic reaction, a stimulus is therefore needed even if the ΔG is of a large negative value. However, high energy mixtures at times do ignite spontaneously leading to disastrous fire and accidents. Composition ME 438, a binary mixture of lead chromate and magnesium in the ratio of 80:20, has shown two such mysterious ignitions resulting in disastrous explosions. The effect of Tammann temperature and moisture on the reaction characteristics of the composition leading to energetically favourable condition of spontaneity is investigated and the results are presented in this paper.

FORMULATION AND STORAGE STUDIES ON HYDRAZINE-BASED GELLED PROPELLANTS

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The current trend in the area of high energy storable liquid rocket propellant research, is to develop gelled/metallized systems and to explore feasibility of their application in liquid rocket motors. The idea stems from the fact that the conversion of a conventional liquid propellant to a gelled state and its subsequent metallization has the potential to significantly enhance the performance and density specific impulse. However, it is mandatory that the gelation of the liquid propellant be brought about with a minimum concentration of gellant and the gel formed should show a shear thinning behaviour and good storage life.

Keeping this in view, an experimental program to prepare thixotropic gels of hydrazine and its methyl-substituted derivatives like monomethyl hydrazine and unsymmetrical dimethyl hydrazine under ambient conditions was conducted. The gellants investigated included particulate, chemical and synthetic materials. The gelation of the liquid fuels could be brought about with gellant concentration as low as 1 wt % in some cases. Metallized gels using up to 40 wt% of Al/Mg metal powders could be formulated. These heterogeneous systems showed a reduction in critical gellant concentration with degree of metallization. Further, less gelation time is observed if the gellant concentration is kept fixed and metal content increased. The storage studies on gelled systems conducted over a period of 3 months showed good stability. The metallized systems, however, showed the settling of metal powders in meagre concentration which does not pose a major problem as these gels could be rehomogenised with stirring.

SYNTHESIS OF AZIDOPOLYESTERS

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Elastomeric binders are used as matrix in which fuel and oxidizers are dispersed in solid propellants. Maximum energy can be achieved from a solid propellant if the binder burns along with the fuel material to release as much energy as possible. This achievement of binder energy value must be consistent with the necessary characteristics of a binder, such as good elastomeric properties and high mechanical strength. The energy of binder can be increased by the introduction of energetic groups like azido, nitro and nitrato groups into the polymer structure. Linear azidopolyesters appear suitable as high energy binders in explosive systems. We have prepared and characterized the chloropolyesters and then azidized them to obtain the azidopolyesters.

This paper presents the characterization data obtained for the chloro and azidopolyester viz. $\overline{M}n$, $\overline{M}w$, MWD, equivalent weight, % Cl, % N etc. and sensitivity data generated on friction and impact, decomposition temperature as well as the deflagration temperature etc. The isocyanate-cured azidopolyester - polyurethanes have been tested for their tensile strain behaviour, freezing temperature, chemical stability and safety.

SYNTHESIS AND CHARACTERISATION OF POLY (AMINO TRINITRO PHENYLENE)

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Supersonic aircrafts, missiles and space exploration require new heat resistant explosives, because explosives stores carried externally on high speed aircraft at low altitudes are subjected to aerodynamic heating, resulting in higher temperature of the explosive filling. For such applications, conventional explosives (TNT, PETN, RDX etc.) are unsuitable and there is a need for thermally stable explosives which are insensitive and capable of being readily formed into the various shapes and have sufficient strength under severe thermal and impact conditions.

Polynitropolyphenylene (PNP) is a unique example of a thermally stable explosive, which exhibits self-binding and film-forming characteristics. These qualities give PNP an edge over comparable thermally stable explosives. With a view to increase thermal stability of PNP, an amino group was introduced into it, as amination has been known to enhance the thermal stability.

The present paper describes the synthesis, characterisation and evaluation of Poly (aminotrinitrophenylene) (PATNP). Synthesis of the amino derivative was accomplished in more than 70% yield by the reaction of hydroxylamine hydrochloride on PNP. Unreacted PNP was removed by solvent extraction. The aminated product was then purified by repeated precipitation in solvent-nonsolvent system and characterised by IR and VPO. IR showed amine stretching frequency at 3370 cm. The DTA decomposition peak temperatures, Tmax were in the range of 450 to 550°C, probably due to some variation in the molecular weight from batch to batch. Impact heights for 50% explosion on a comparative scale, for PNP and PATNP were 58 & 77 cm and friction sensitivity was 28.8 & > 36 kg respectively.

SAFETY AND AGEING

APPLICATION OF QUANTITATIVE HAZARD ANALYSIS TECHNIQUES IN MIXING OPERATIONS OF HIGH ENERGY MATERIALS

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Production of composite propellants involves a variety of operations and processes, of which mixing of various ingredients is a key step. The ingredients generally include oxidizers, fuels, polymeric binders, curing agents, bonding agents, plasticizers, stabilizers, crosslinking agents and catalysts. Given the intrinsically hazardous nature of many of these ingredients, mixing operation, which is carried out in a stepwise manner with carefully weighted ratios of the reactants, under controlled conditions, is still one of the most hazardous steps in the production process.

In this paper, quantitative assessment (QA) of the hazards involved in such a mixing operation has been carried out using Fault Tree Analysis (FTA) techniques to identify all the possible basic event combinations which could lead to the occurrence of a selected 'Top Event' such as fire or explosion in the Mixer Building. The likelihood of occurrence of such an event, has been calculated and classified as marginally hazardous under TNO system of classification.

Some recommendations to improve the safety of the mixer section based on results of the FT & ST analysis are suggested. Using a Safety Tree, which is the logical reverse of the fault tree, those events which would prevent or reduce the probability of occurrence of top event have been identified and ways and means of reducing these hazards to acceptable levels have also been suggested. The paper presents these recommendations, as well as results obtained to approximate order of magnitude of improvement in safety, if these recommendations are implemented.

ELECTROSTATIC HAZARDS TO ROCKETS AND MISSILES

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Electrostatic accumulation and discharges often cause accidents as gases, vapours, aerosols and airborne dust can be ignited by small invisible electrostatic sparks in fuel. Thus, explosives, pyro devices, solid propellant rocket motors and liquid propellants need full fledged protection against electrostatic accumulation and discharge.

The aim of this paper is to bring out safety awareness about electrostatic hazards among the personnel who are handling solid propellants, liquid propellants (fuel), electro explosive devices and sensitive electronic control equipment. Case studies are also discussed to highlight hazards of missiles and rockets ignition due to electrostatic discharges. The paper also deals with the mechanism of electrostatic charge generation and tests carried out on the ignition of squibs of electro explosive devices due to electrostatic discharge by human beings.

HAZARD CLASSIFICATION TESTING OF PRIMERS USED IN SMALL ARMS AMMUNITION

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Primer forms an important part of an explosive train in an ammunition round. It is a small initiating device used for ignition of propellant charge and subsequent ejection of projectile from a weapon. It contains a small amount of sensitive composition, the output of which is of sufficient magnitude to ignite the propellant charge. Hitherto because of their low charge mass, the primers were considered as belonging to safety class.

Recent serious accidents involving primers raised doubts about their present hazard classification under safety class. Therefore, a comprehensive test programme was undertaken to conduct field trials with different types of primers to ascertain their true behavior under different conditions.

The data on different types of primer compositions used for filling was collected. The analysis showed that two main types of compositions used for primer filling are based on either mercury fulminate or lead styphnate along with other additives. To generate maximum data, trials were conducted with representative compositions selected from these two types. The trials were carried out with primers packed in different types of packages, viz. transit packages (intra factory package for use within the factory for transporting primers from one manufacturing unit to another) and also in final service packages (inter factory package used for transportation of primers from one factory to another). Trials were also carried out to study the bahaviour of primers by varying the charge mass of the compositions.

These trials have brought out that the nature of filling composition, its charge mass and the type of the package used has a profound influence on the hazard classification of the primers. It was observed that the behaviour of the primer changes significantly, viz. from safety class to mass explosion hazard with the change in any of the above parameters. The detailed trial results and conclusions drawn therefrom are presented in this paper.

EFFECT OF ENVIRONMENTAL CONDITIONS ON DIMENSIONAL, PHYSICO-MECHANICAL AND COMBUSTION PROPERTIES OF CCC

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Conventional brass cartridge cases are being replaced by Combustible Cartridge Cases (CCC) for their well known advantages for artillery/tank gun ammunition. However, CCCs are susceptible to moisture due to the presence of ingredients like cellulose and nitrocellulose. This results in dimensional changes and leads to adverse effect on ballistic performance of the ammunition. Hence, a systematic study was carried out to establish the effect of environmental factors namely temperature and humidity on the CCC components.

Dimensional changes are observed during various stages of manufacture and storage. These are quite significant and are very critical for tool design. Further, experiments were carried out with the final combustible liners, where the samples were exposed to varying temperatures and % relative humidity (% RH) for a particular period. These samples were checked for dimensions and analysed for density, tensile strength and subjected to closed vessel firings. Though at ambient temperature there were no significant changes in physical parameters, at -20°C and +55°C appreciable changes were observed. Similarly at 65% RH, changes in these parameters were marginal while the same were of higher magnitude at 75% and 85% RH. Initial experiments revealed that the effects are reversible.

Quantification of the changes in parameters such as dimensions, density, tensile strength and CV data, will not only reduce the chances of rejections, but also improve the quality of the ammunition, since they have a bearing on the overall ballistic performance. In the present paper, attempts were made to quantify the changes in physical and mechanical properties of CCC during process and storage at different conditions.

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